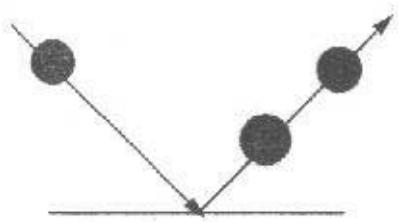
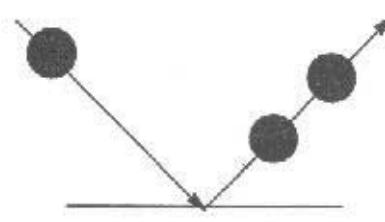


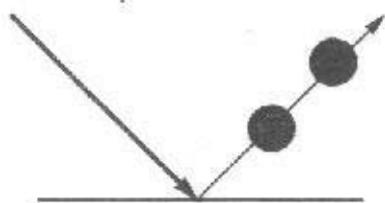
PULSED ATOMS (FAB)



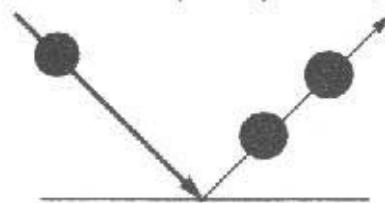
PULSED IONS (SIMS)



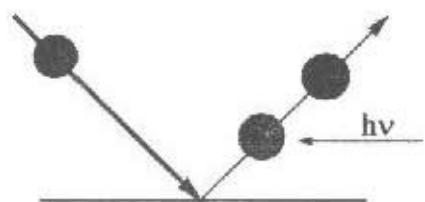
PULSED LASER



PULSED PARTICLES
(PDMS)

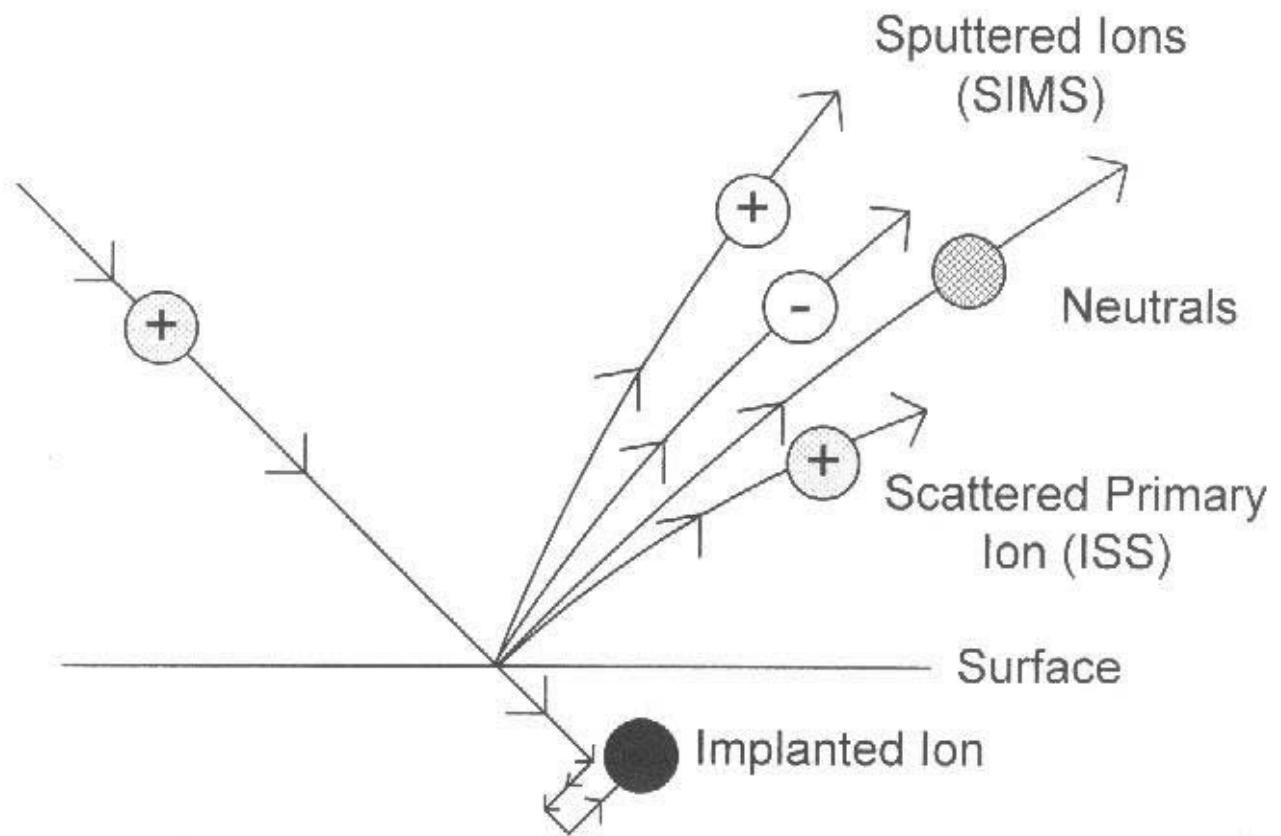


POSITIONIZATION

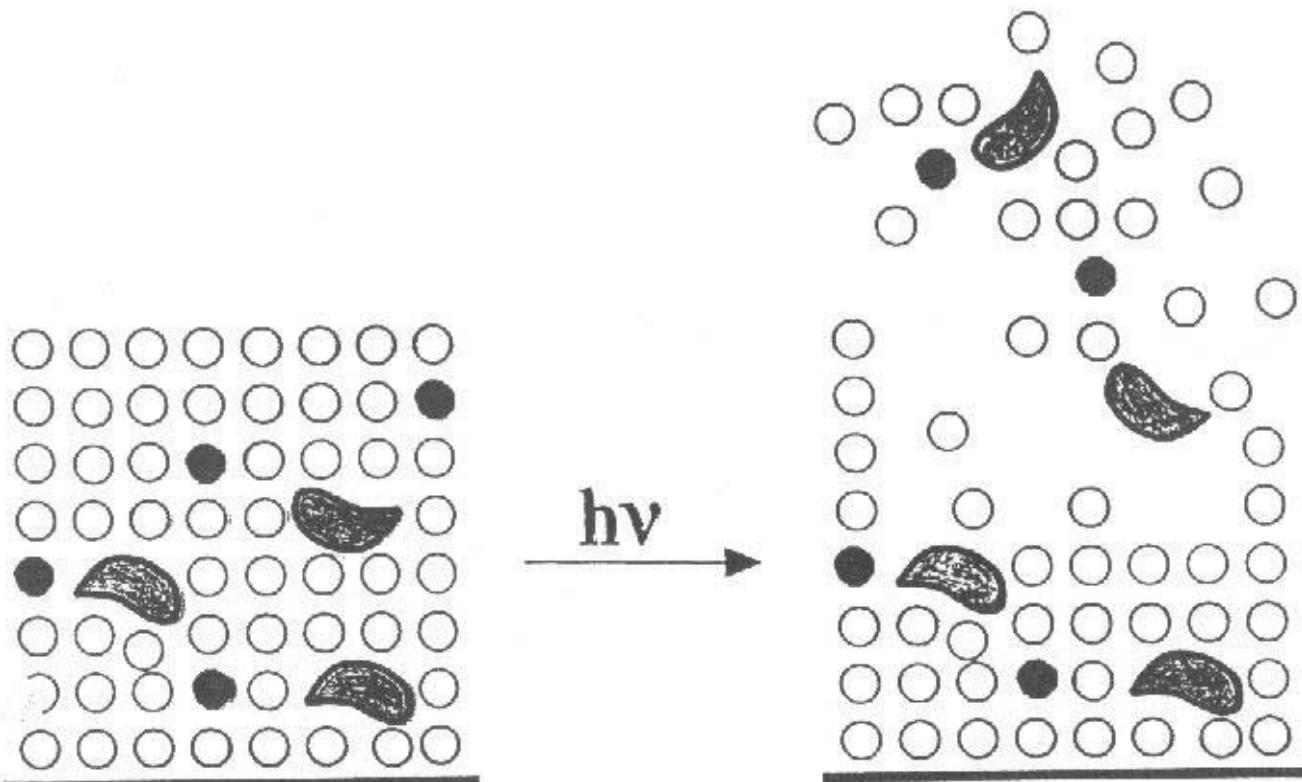


ELECTROSPRAY





Absorption of Laser Radiation by the Matrix Induces a Volume Ablation



 - Analyte

 - Matrix

 - Cation

$(A + H)^+$

$(A + \text{Cation})^+$

Mass Spectrometry Methods For Polymers

MALDI

Little Fragmentation
Simple Spectra

SIMS

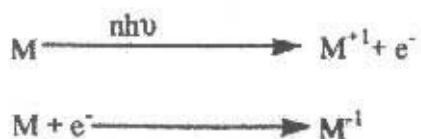
Significant Fragmentation for $M_n > 5000$
Complex Spectra for $M_n > 5000$

Electrospray

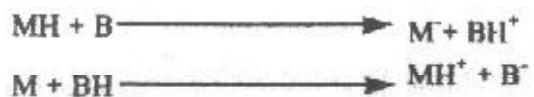
No Significant Fragmentation
Complex Spectra - Multiple Charges

IONIZATION PROCESSES IN SIMS

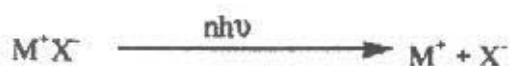
GAIN OR LOSS OF ELECTRONS



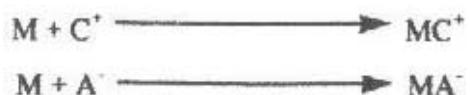
GAIN OR LOSS OF PROTONS

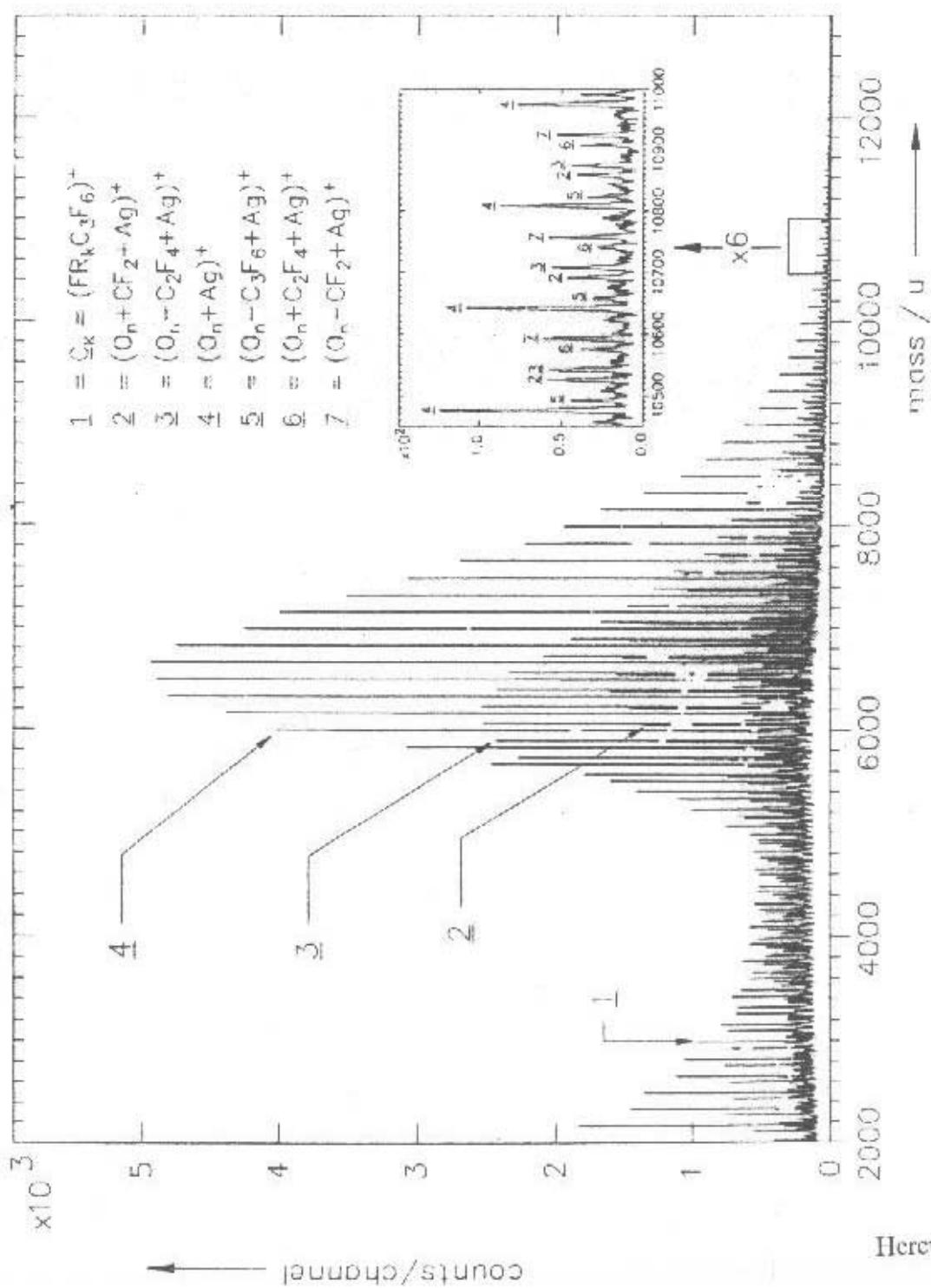


IONIZATION OF SALTS



ION-ATTACHMENT REACTIONS





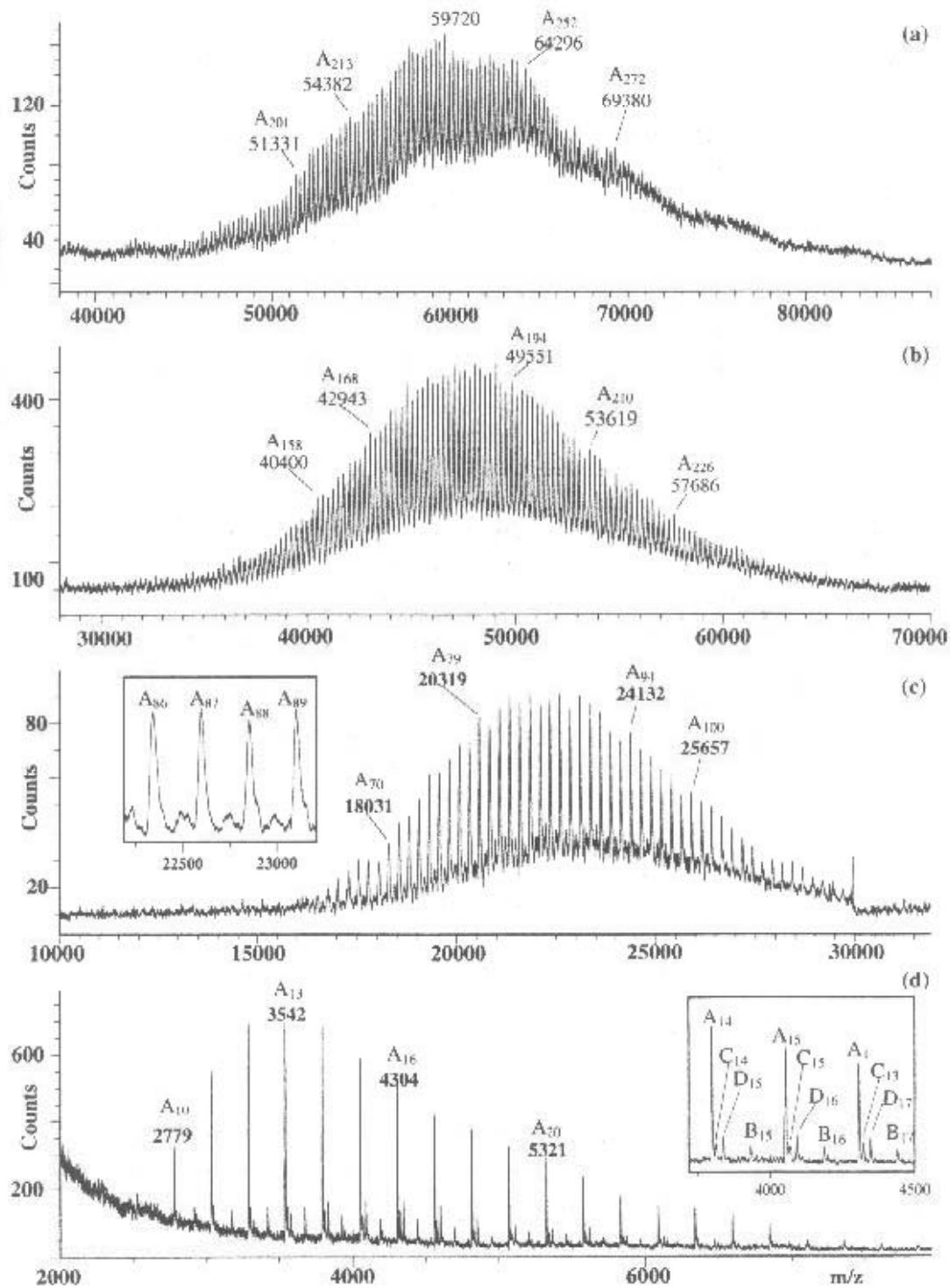


FIGURE 10.26

Positive ions MALDI-TOF mass spectra of the SEC fractions from sample PC1 collected at: (a) 27.8 mL, (b) 28.54 mL, (c) 30.2 mL, and (d) 35.3 mL.

Homopolymers

E-M-M-M-M-M-M-M-M-M-(...)-M-M-M-M-M-M-M-M-M-T

Copolymers

Random:

E-B-A-B-A-A-B-B-A-B-B-A-B-(...)-B-B-B-A-A-B-A-B-A-A-T

Alternating:

E-A-B-A-B-A-B-A-B-A-B-(...)-A-B-A-B-A-B-A-B-A-B-A-B-T

Block Copolymers:

Diblock:

E-A-A-A-A-(...)-A-A-A-A-B-B-B-B-B-(...)-B-B-B-B-B-T

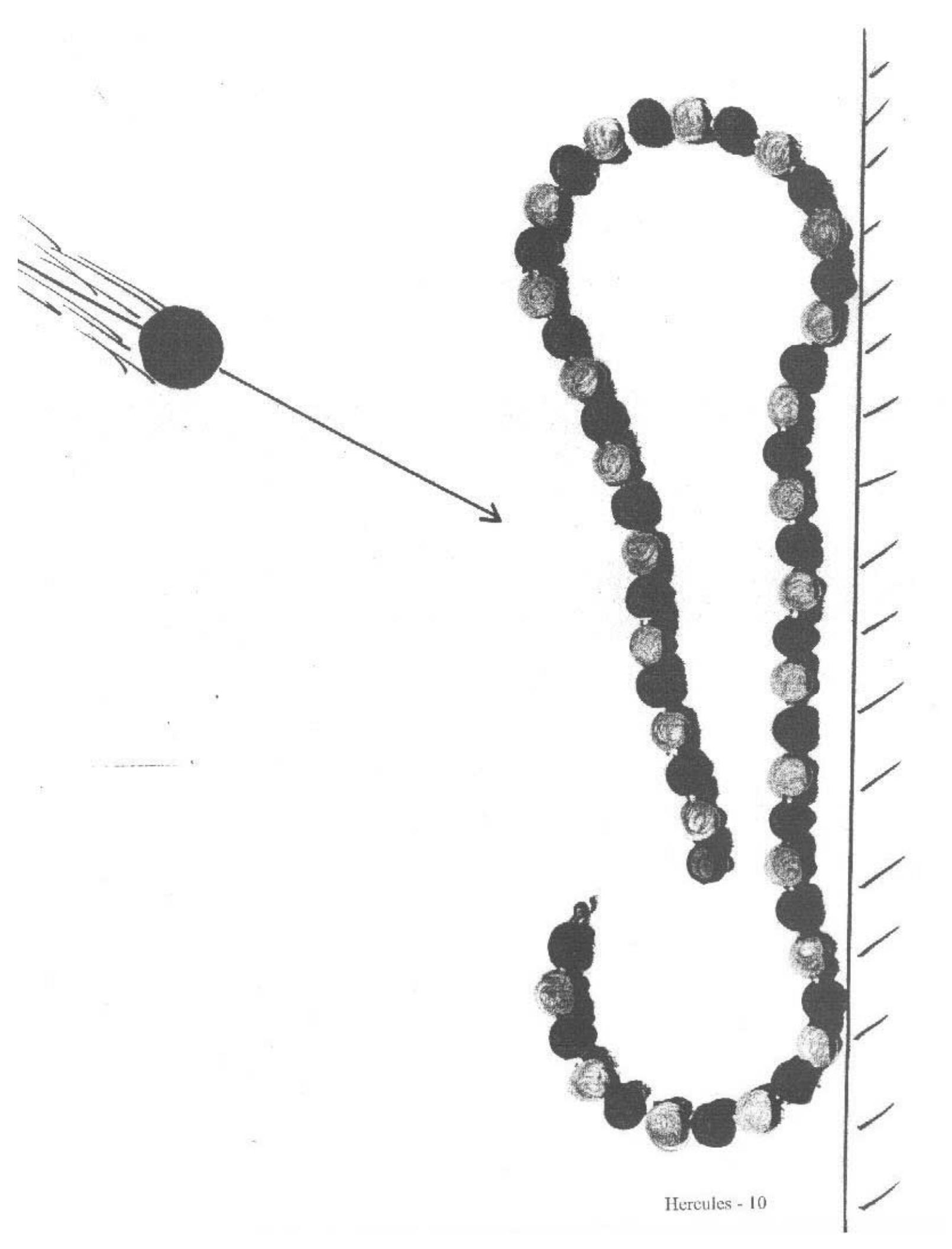
Triblock:

E-A-A-A-(...)-A-A-A-B-B-B-(...)-B-B-B-A-A-(...)-A-A-T

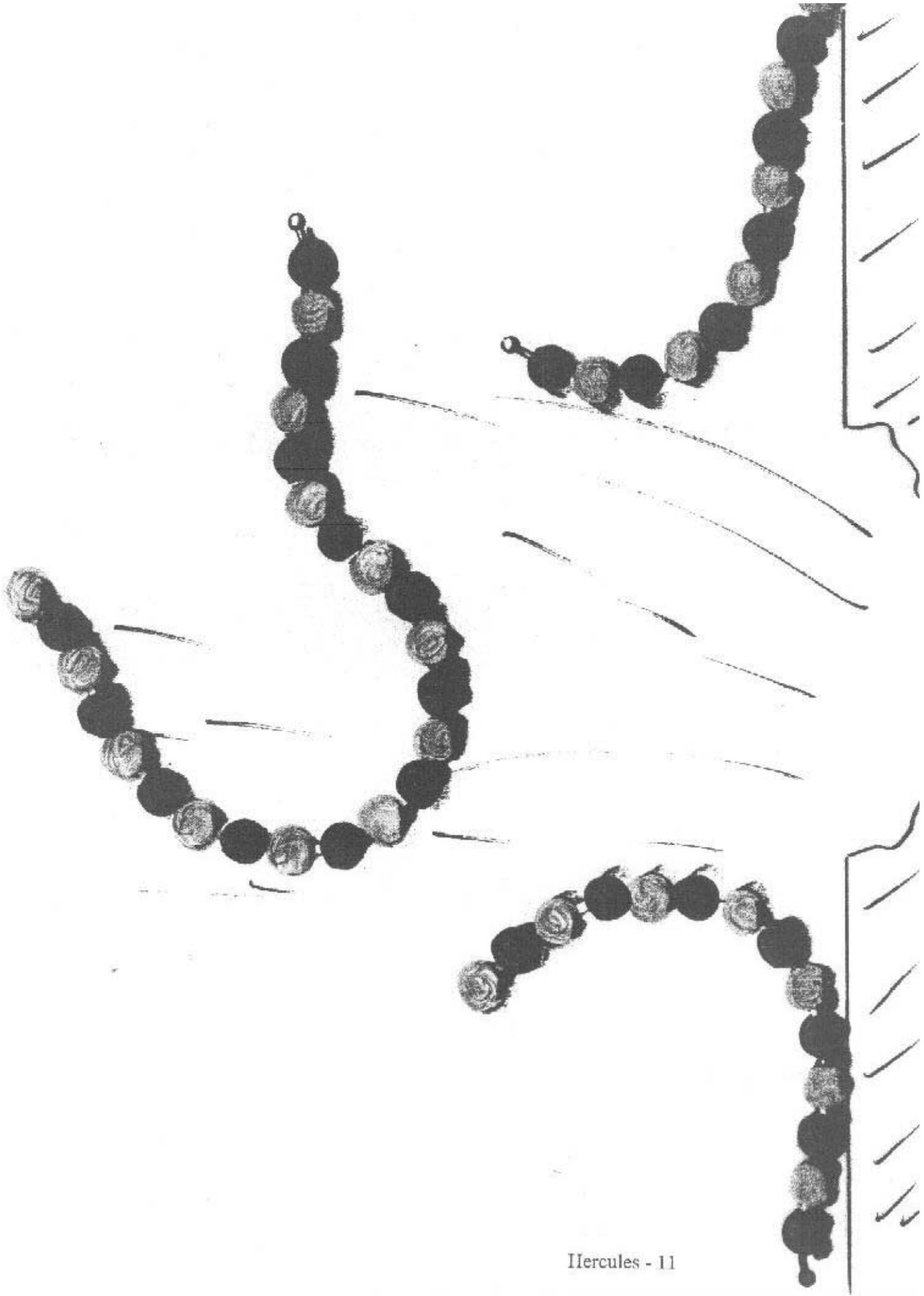
E-A-A-(...)-A-A-B-B-B-(...)-B-B-B-C-C-C-(...)-C-C-C-T

Information About Polymers Which Can Be Obtained By Mass Spectrometry

1. Identification- Repeat Unit(s)
Functional Groups
Terminal Groups
2. Oligomer Distributions and Average
Molecular Weights
3. Order of Repeat Units and/or Blocks in
Chains
4. Crosslinking and/or Branching
5. Stereoregularity
6. Surface Segregation in Block
CoPolymers



Hercules - 10



Hercules - 11

TYPES OF IONS FORMED IN TOF-SIMS

1. OGLIMERS

M/Z < 12,000



2. FRAGMENT IONS

M/Z < 5,000

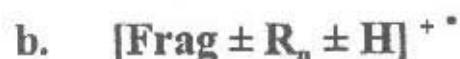
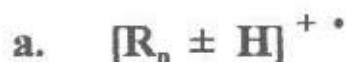
a. With Terminal Group



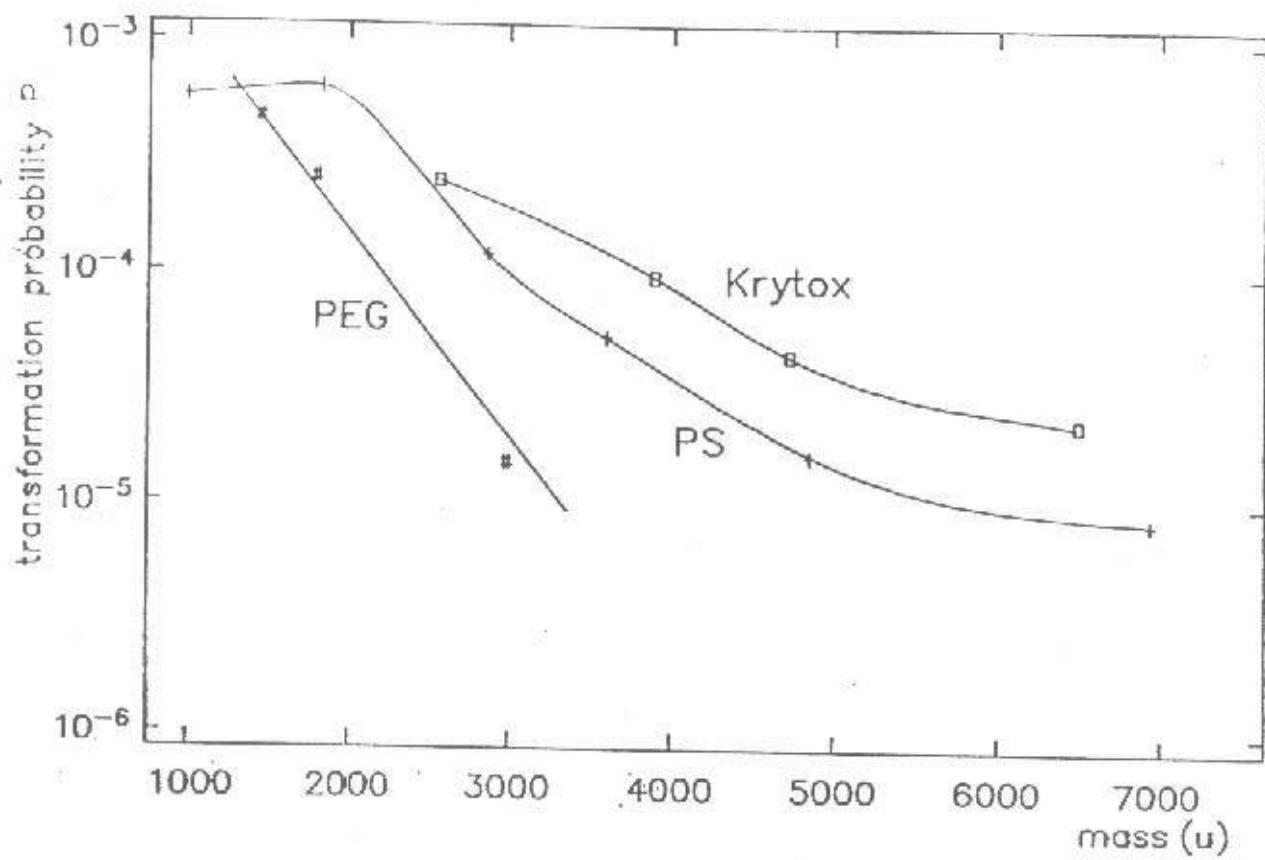
b. Chain Fragment



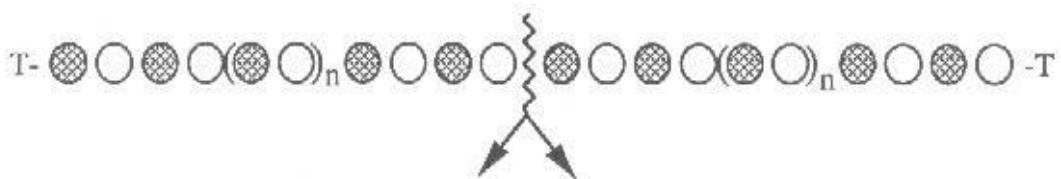
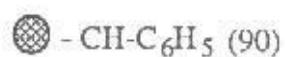
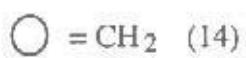
3. SMALL FRAGMENT IONS M/Z < 500



Transformation probability P of cationized oligomers



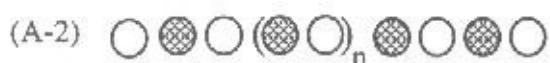
- decrease of P by 1-2 orders of magnitude
 - for PS and Krytox between 2000 u and 7000 u
 - for PEG between 1000 u and 3500 u



↓ Path A



Mass = R_n



Mass = $R_n + \bigcirc (\Delta)$



↓ Path B



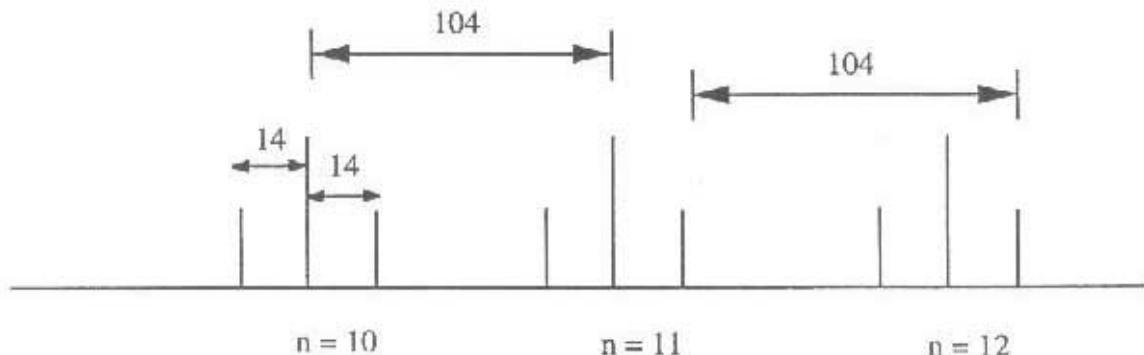
Mass = R_n

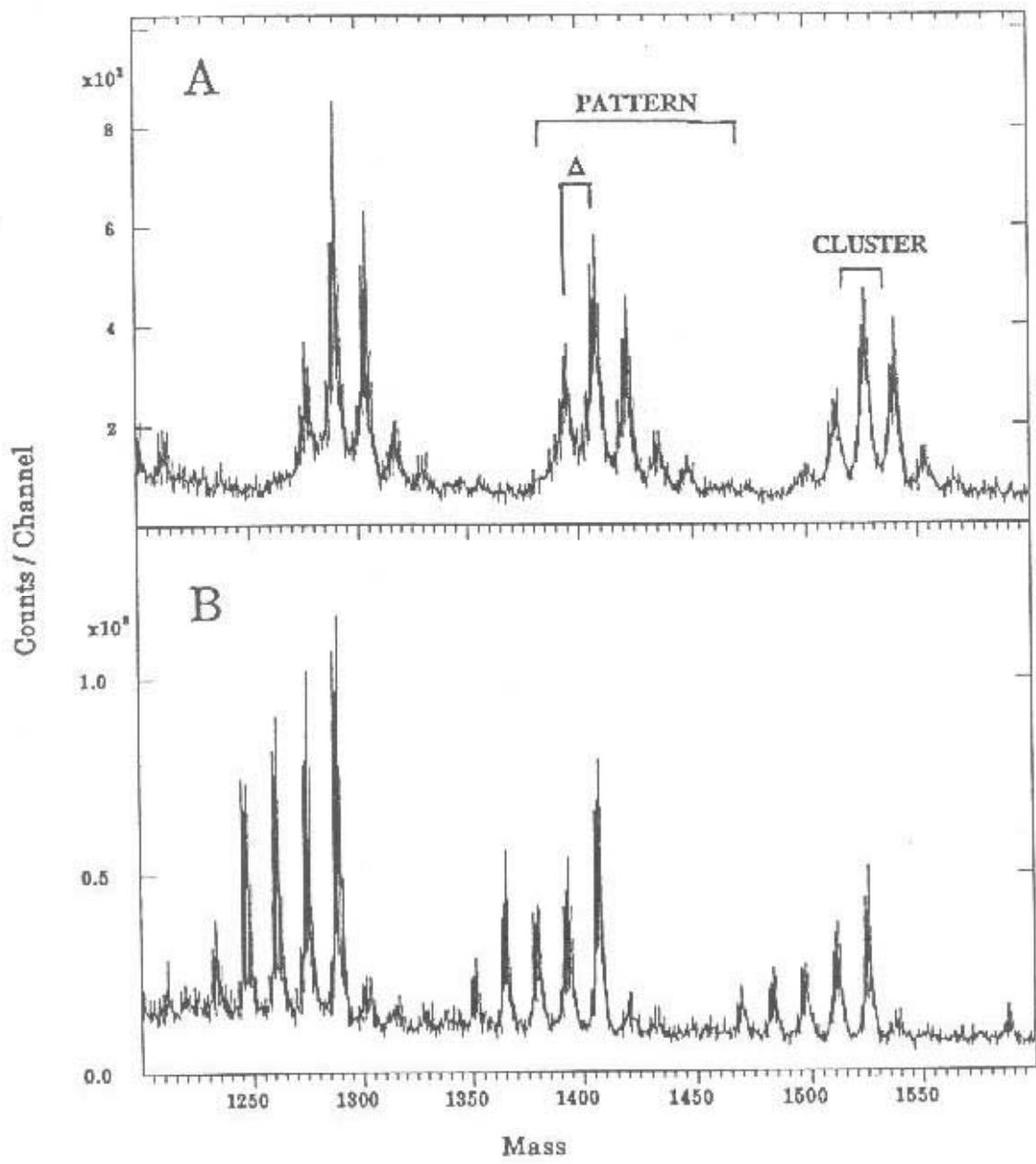


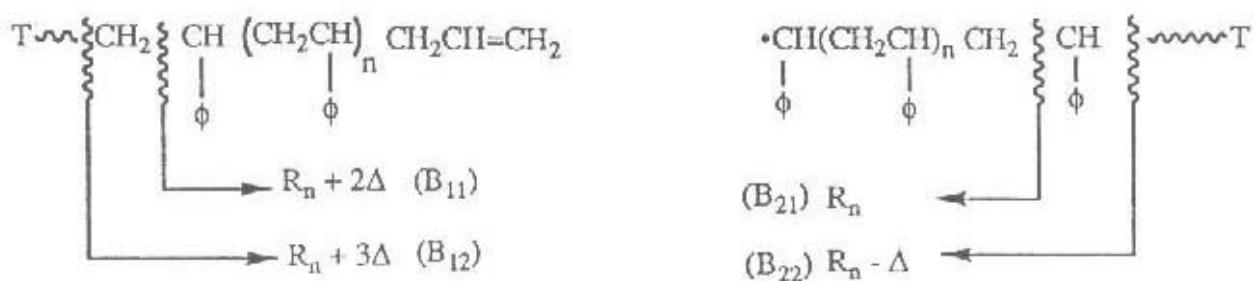
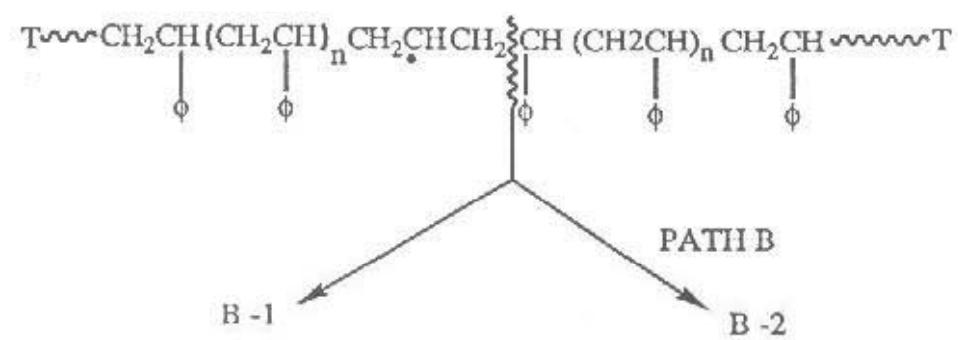
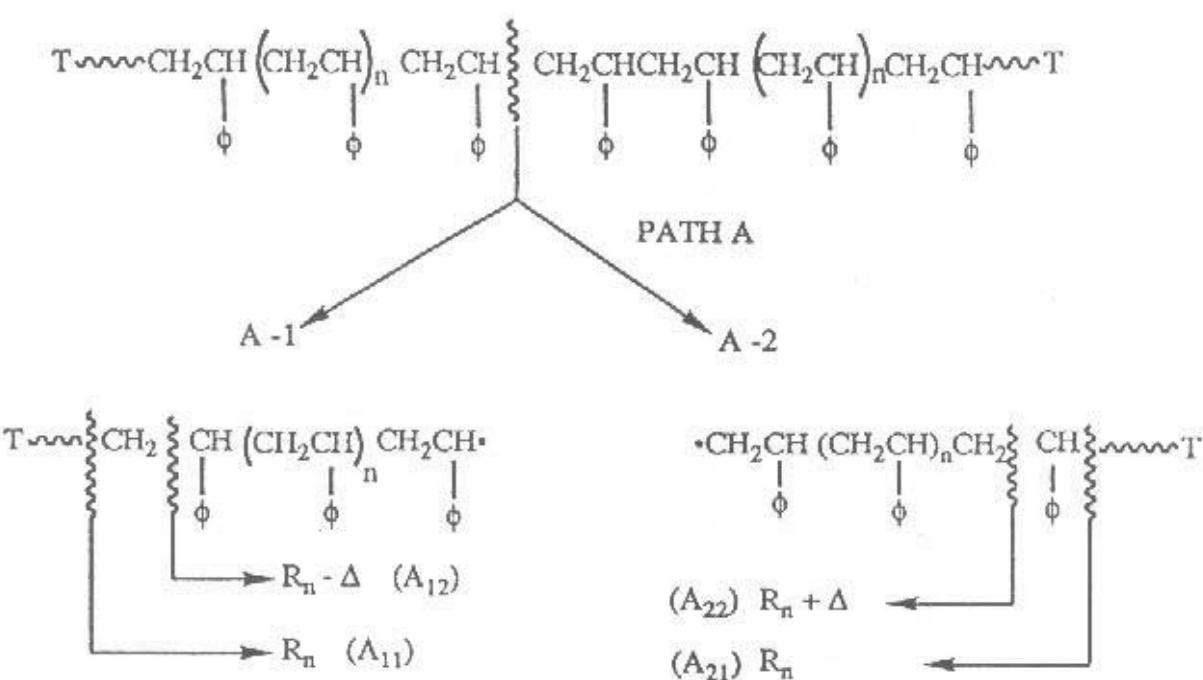
Mass = $R_n + \bigodot (\Delta)$

Mass = $R_{n+1} - \bigcirc (\Delta)$

For $n = 10 - 12$







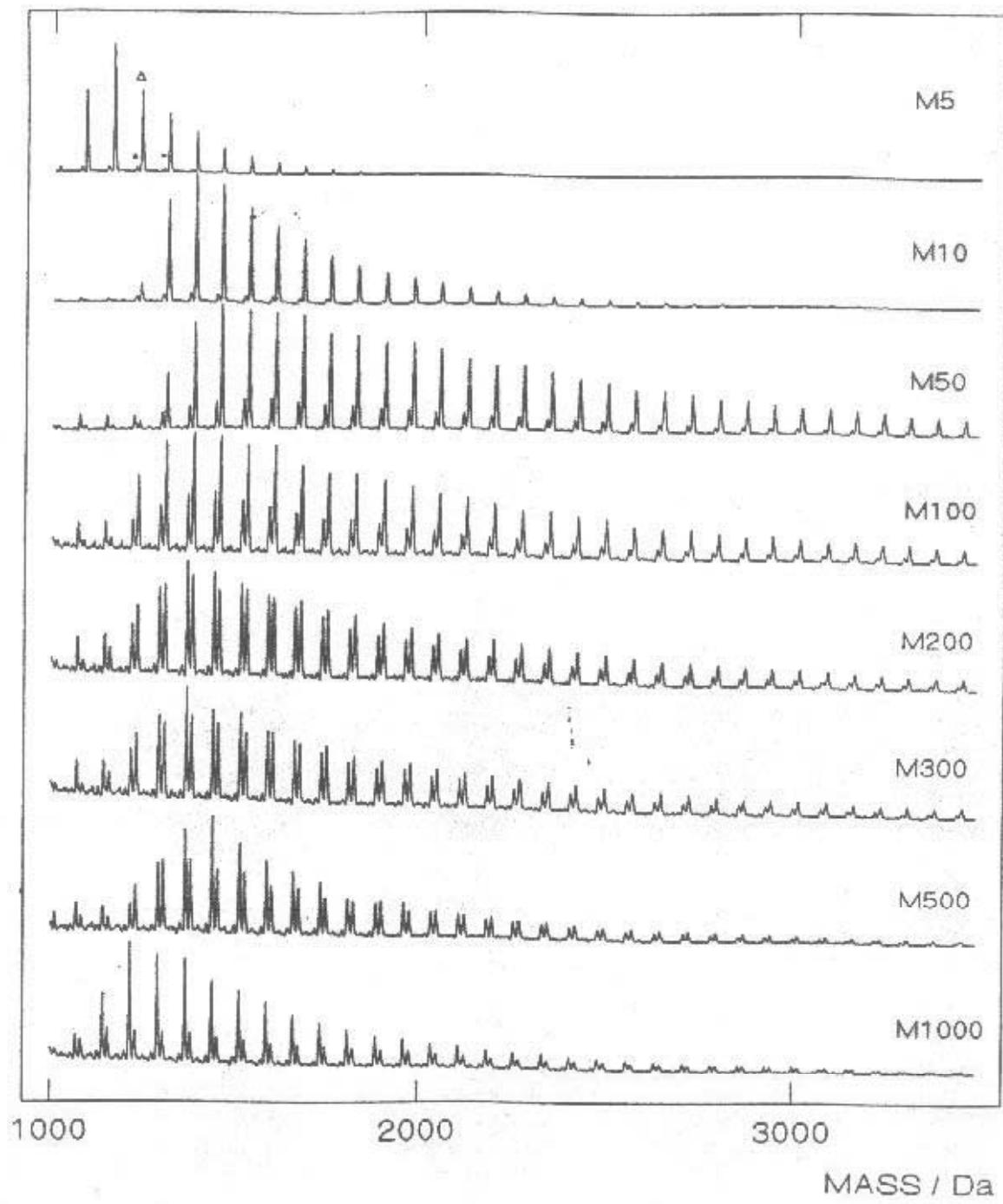
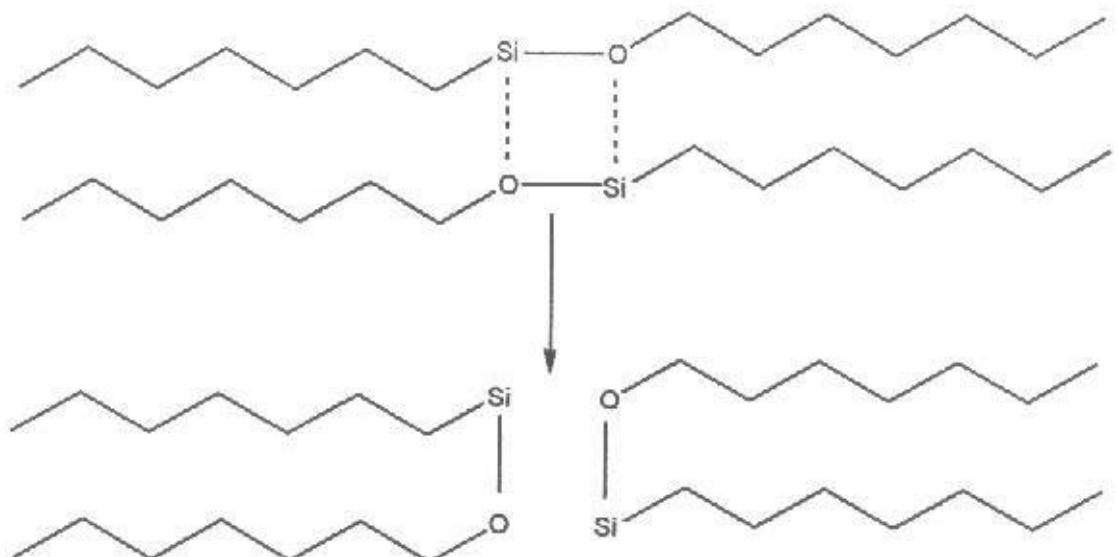


Figure 10: Mass Region from 1000-3500 Da for PDMS

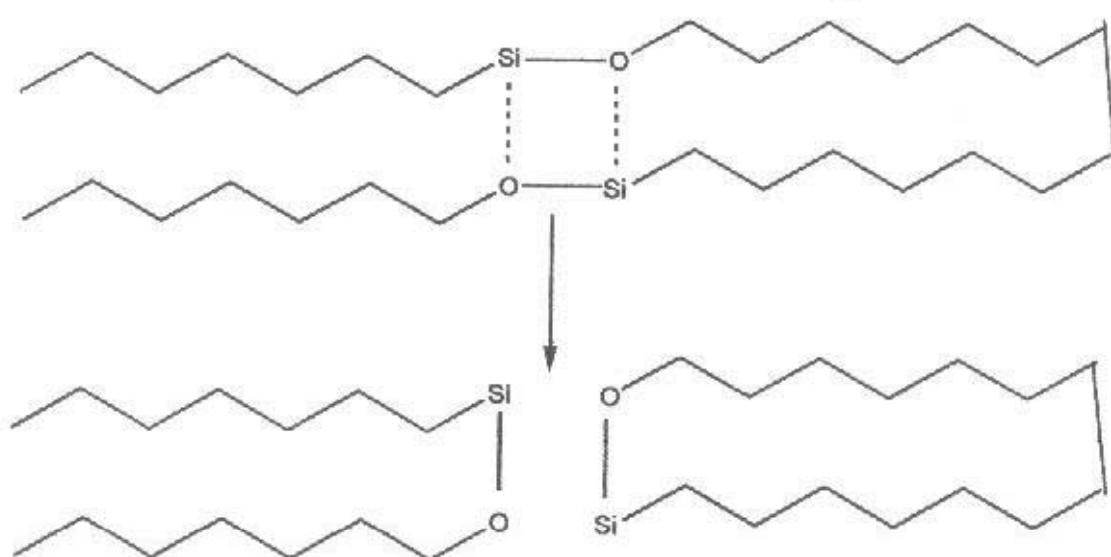
* $[R_n + Ag]^+$

Δ $[nR + 14 + Ag]^+$



Linear Segment

Linear Segment

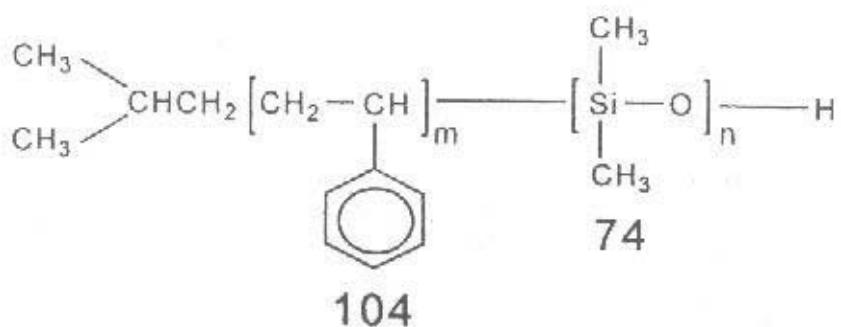


Linear Segment

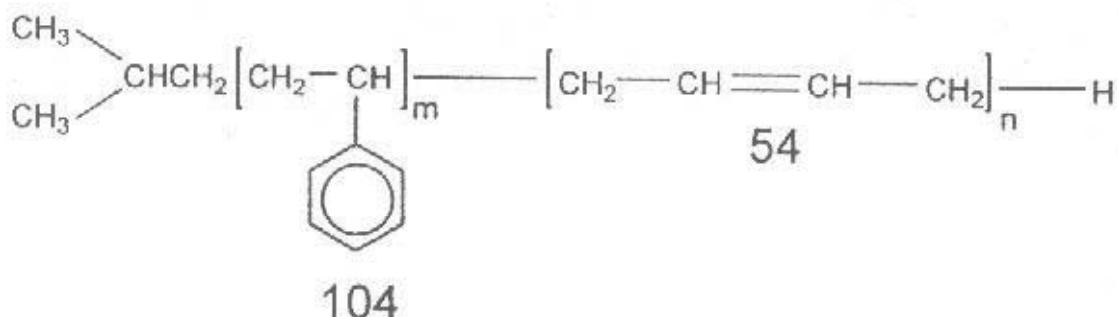
Cyclic Oligomer

Structure of Diblock Copolymers

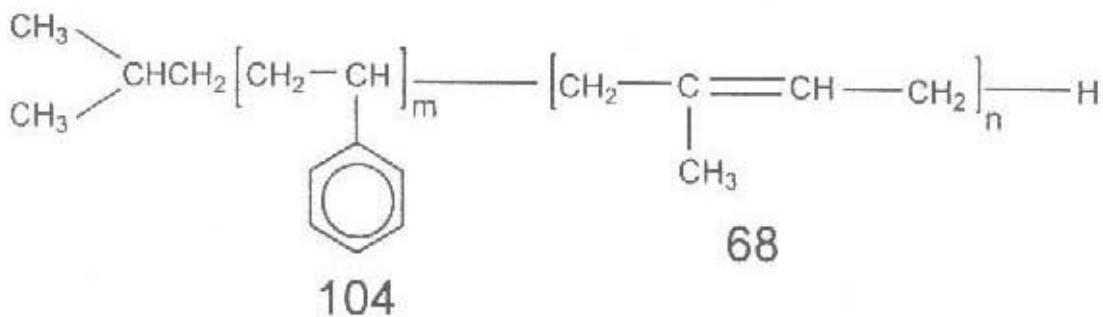
Polystyrene-Polydimethylsiloxane

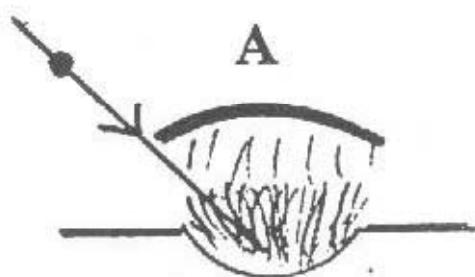
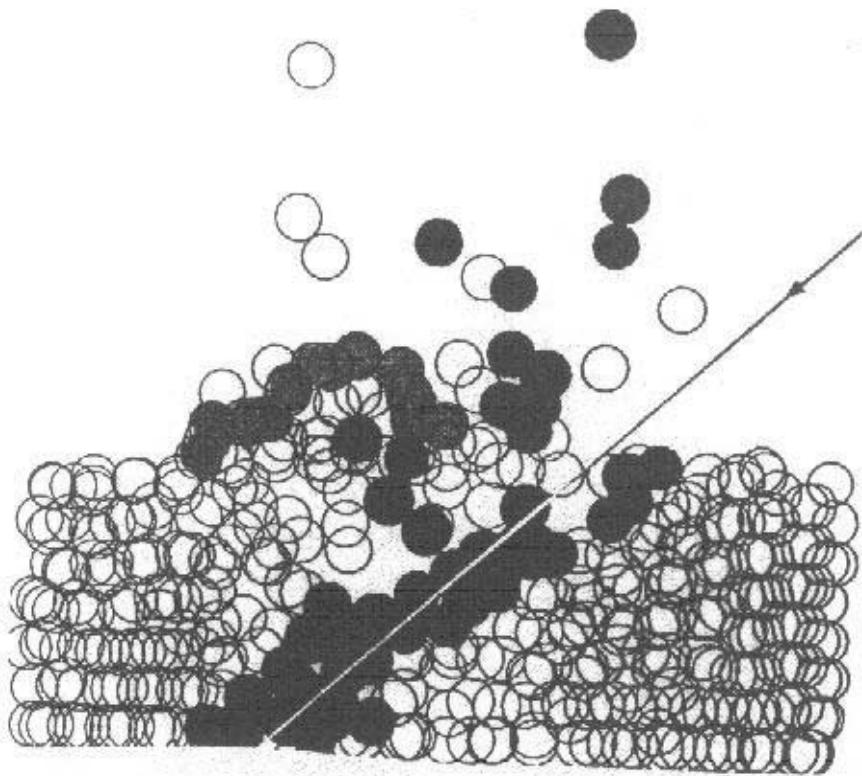


Polystyrene-Polybutadiene

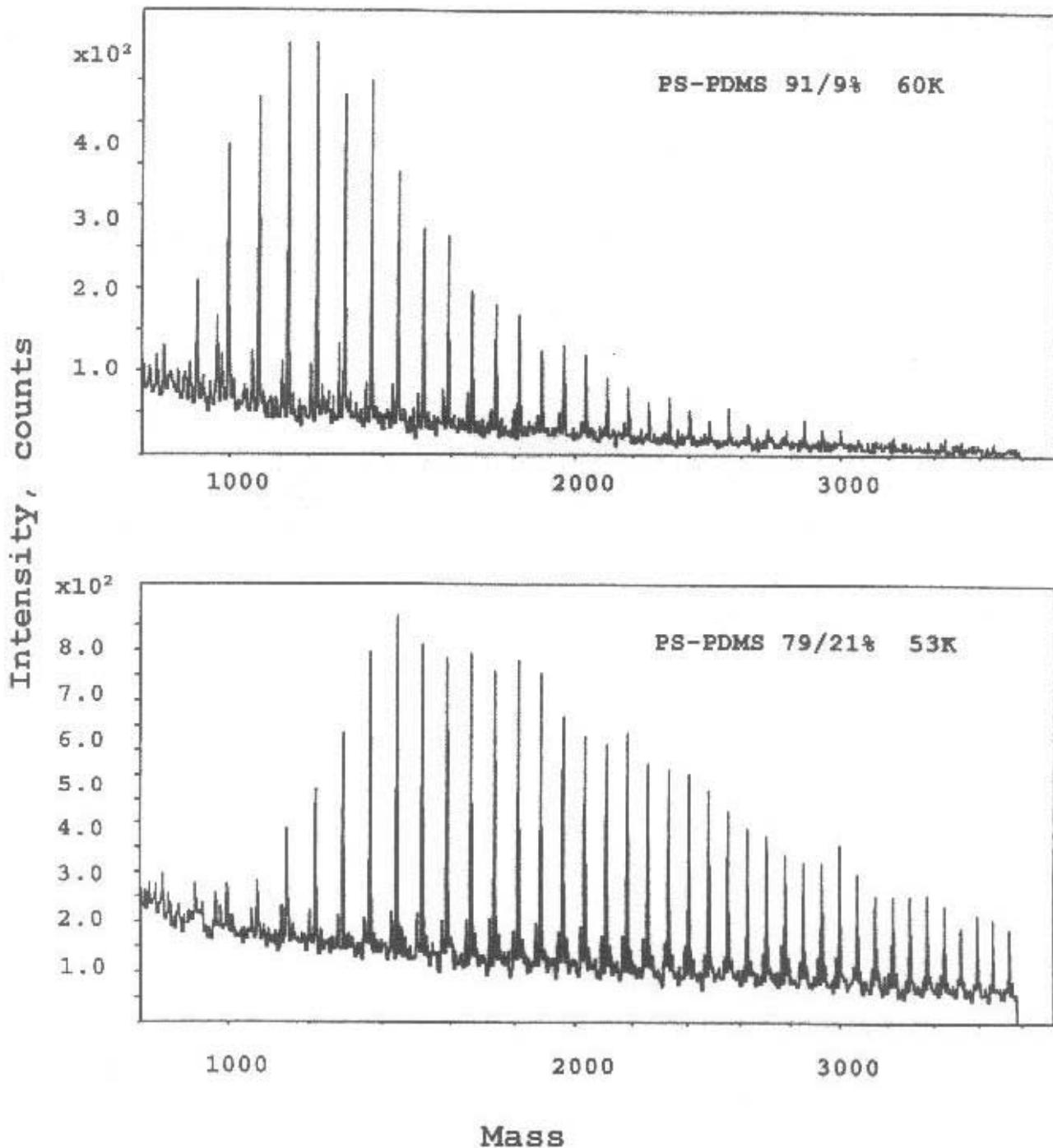


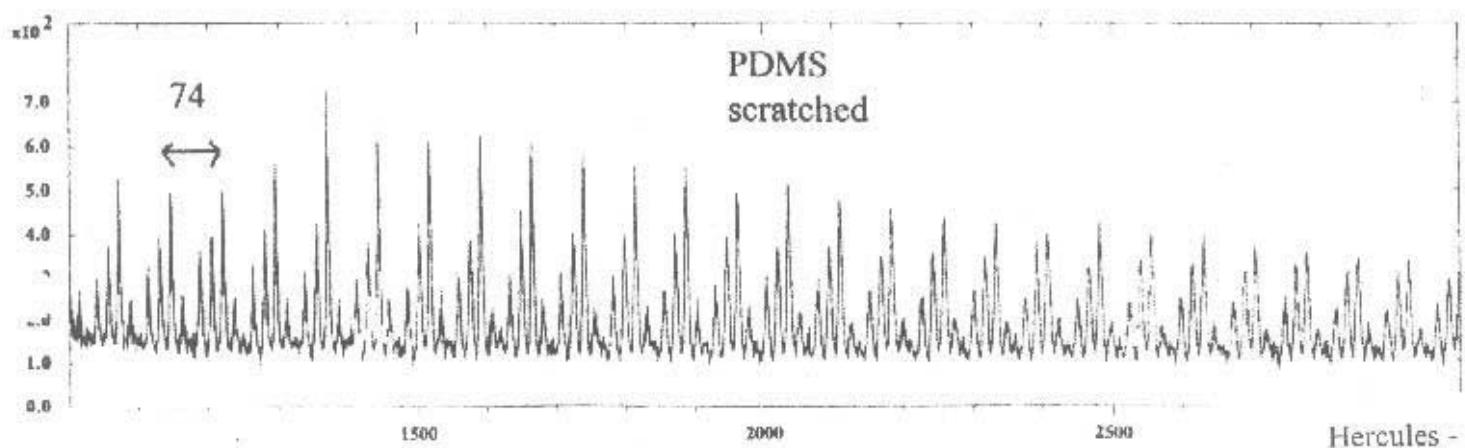
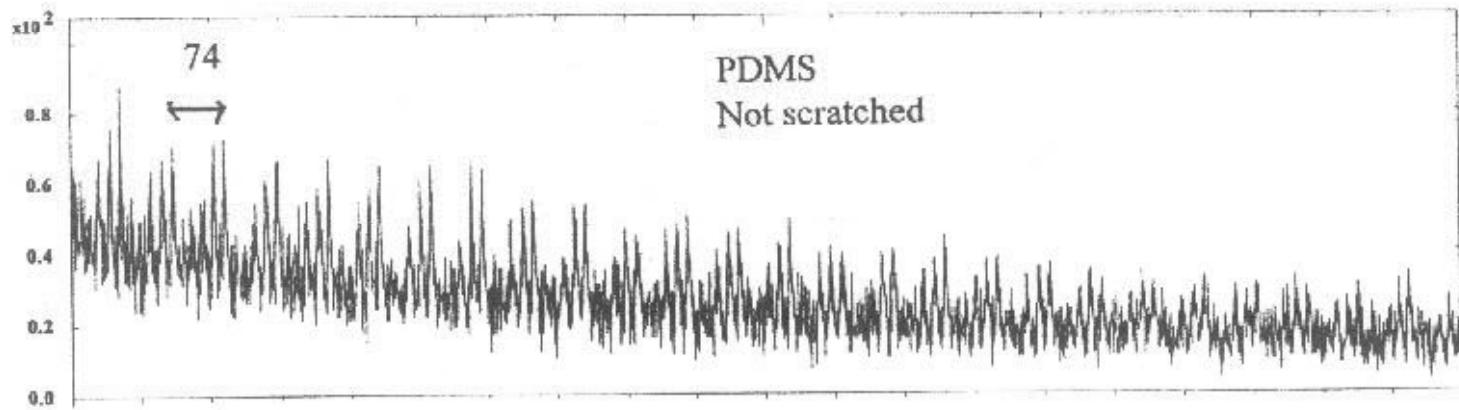
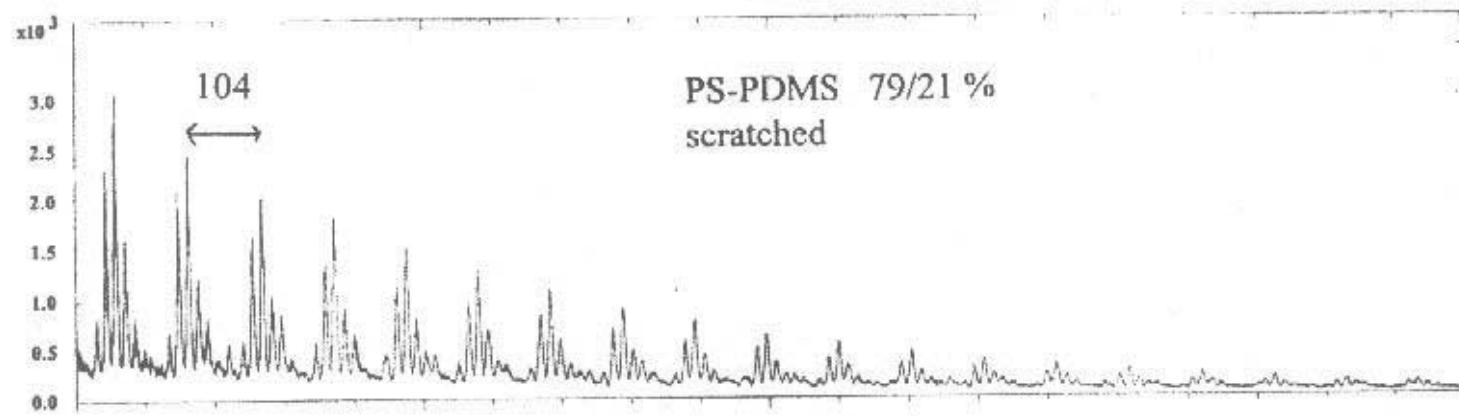
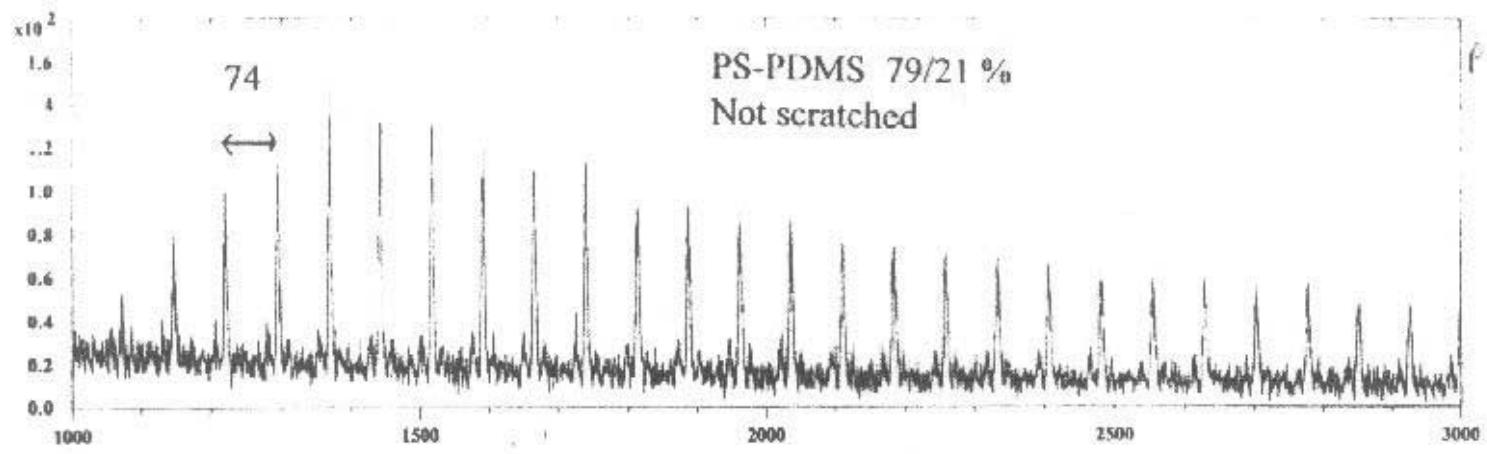
Polystyrene-Polyisoprene





Polystyrene-Polydimethylsiloxane





BLOCK COPOLYMERS

What can cause a SIMS spectrum showing only ONE compound?

1. Surface Segregation
2. Unequal Ion Yields

RELATIVE SECONDARY ION YIELDS FOR PDMS : PMPhS MIXTURES

Mixture (1:2) - 2.8 ± 0.5

Mixture (1:5) - 3.3 ± 0.5

Absolute Ion Yields:
PDMS 9×10^{-5} ($\pm 28\%$)
PMPhS 5×10^{-5} ($\pm 44\%$)

RELATIVE ION YIELD IS 1.8

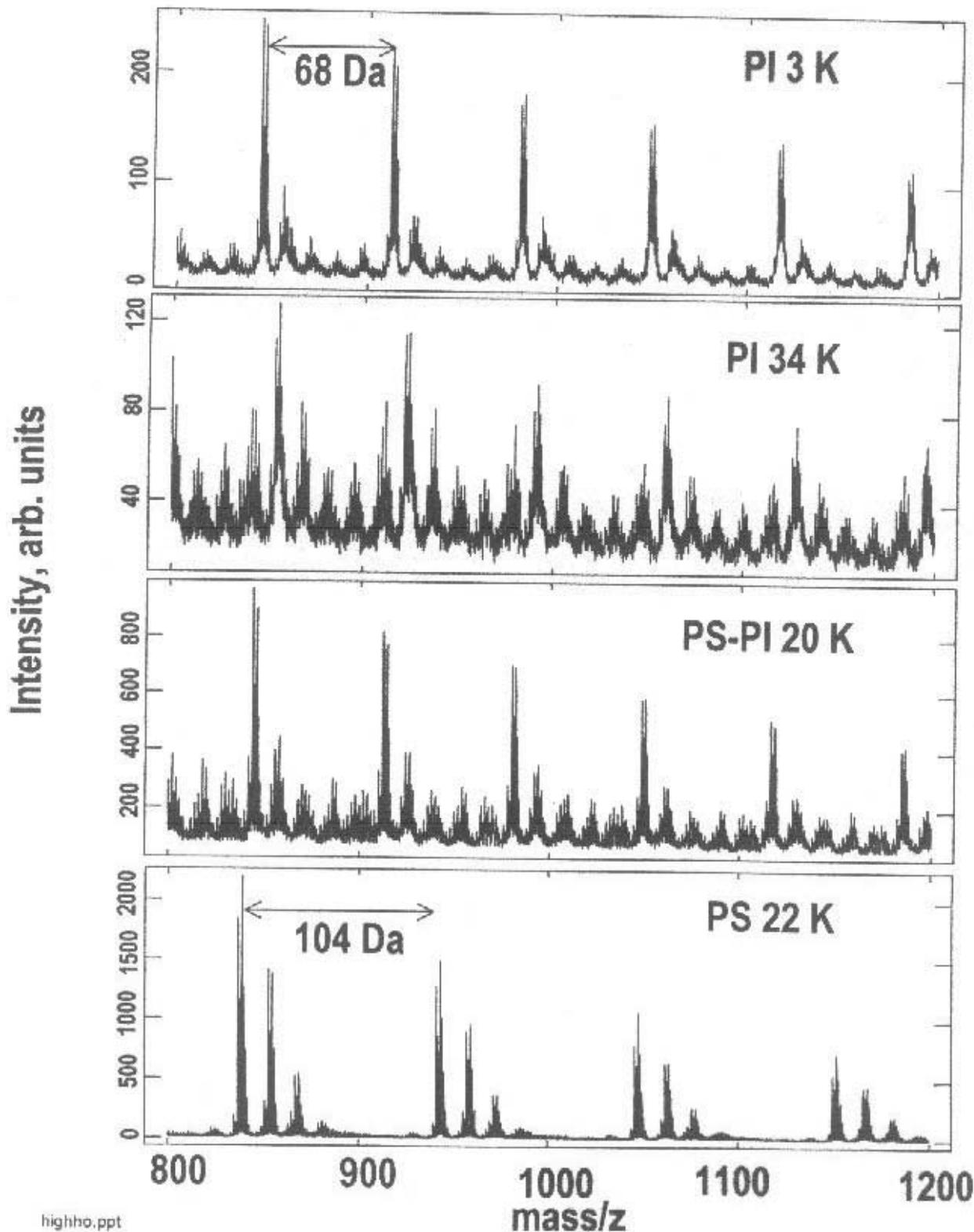
Relative Ion Yield of Polystyrene to PDMS is 3

Relative Ion Yield of Polystyrene to Polyisoprene is 9

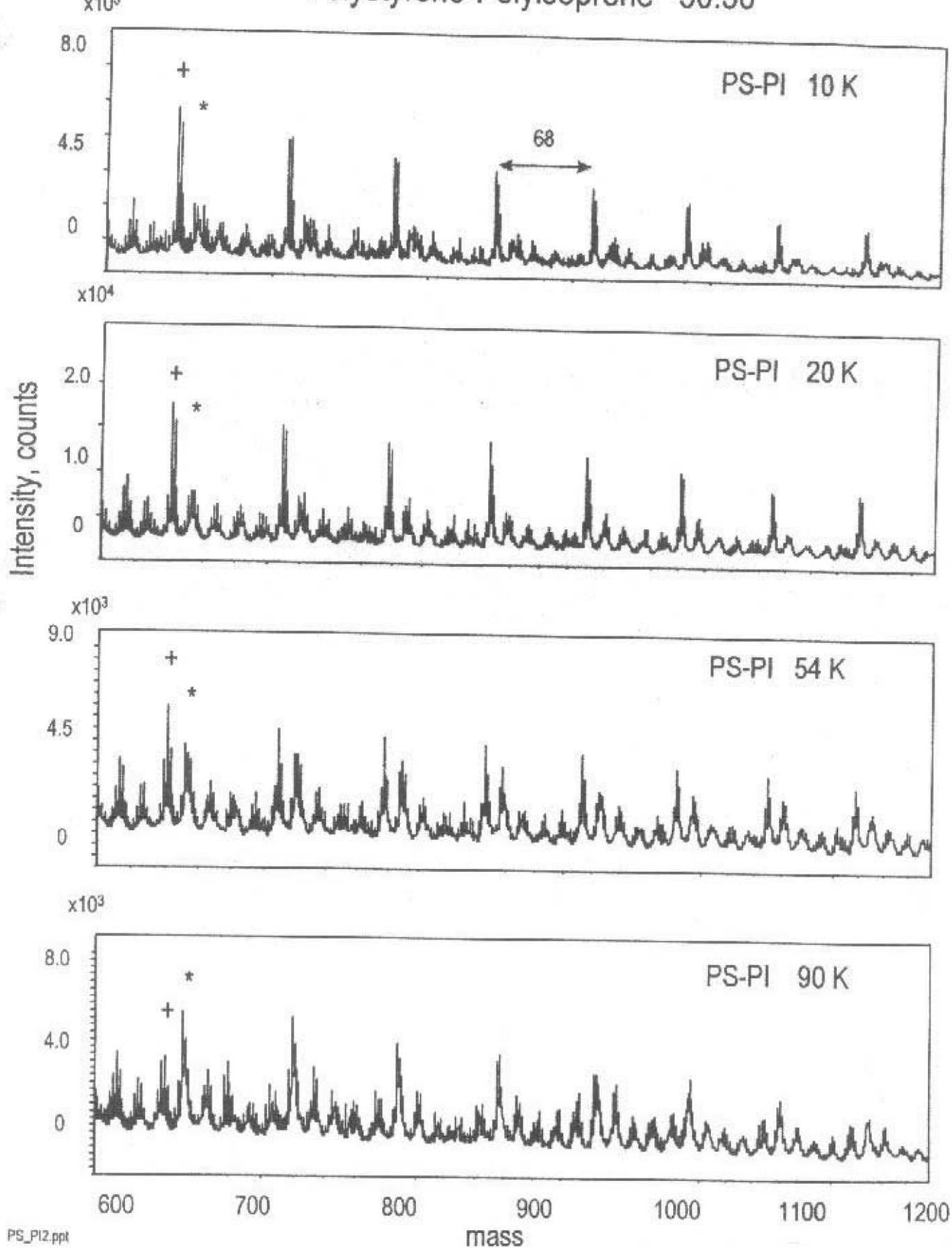
Calculated Absolute Ion Yield for Polystyrene is 3×10^{-4}

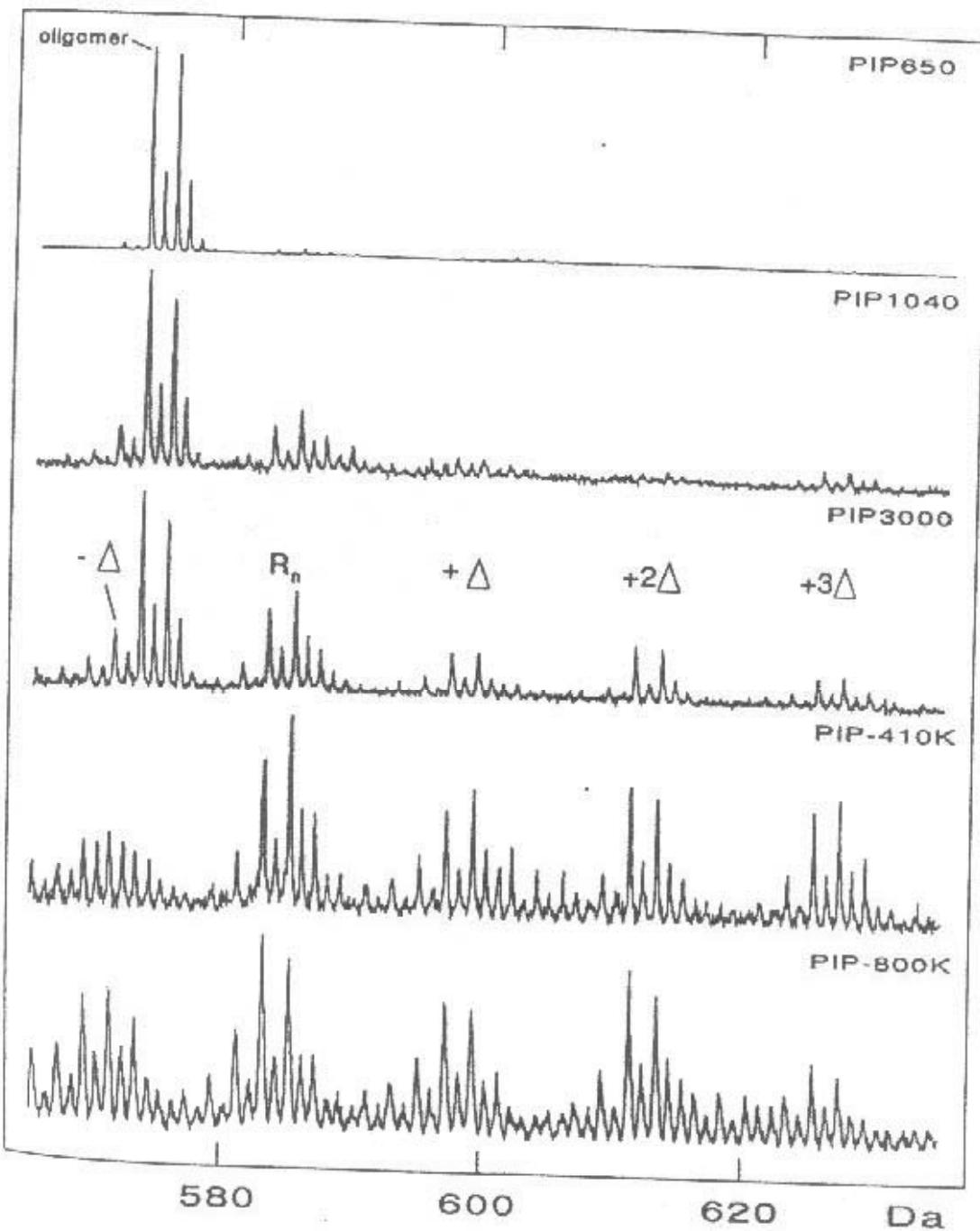
Literature Value for Polystyrene is 6×10^{-4}

High-mass TOF-SIMS spectra: PS-PI diblock copolymers and homopolymers

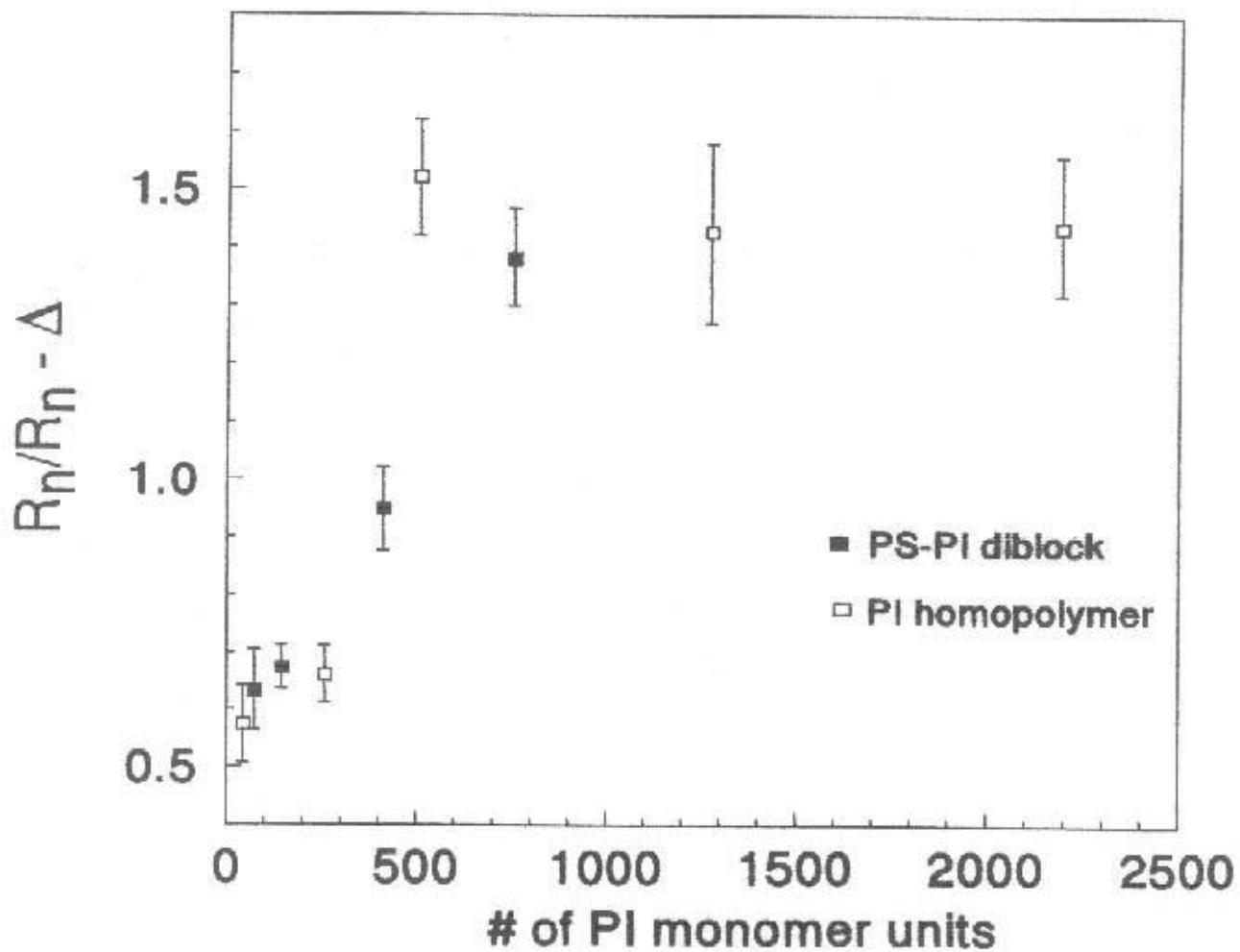


Polystyrene-Polyisoprene 50:50

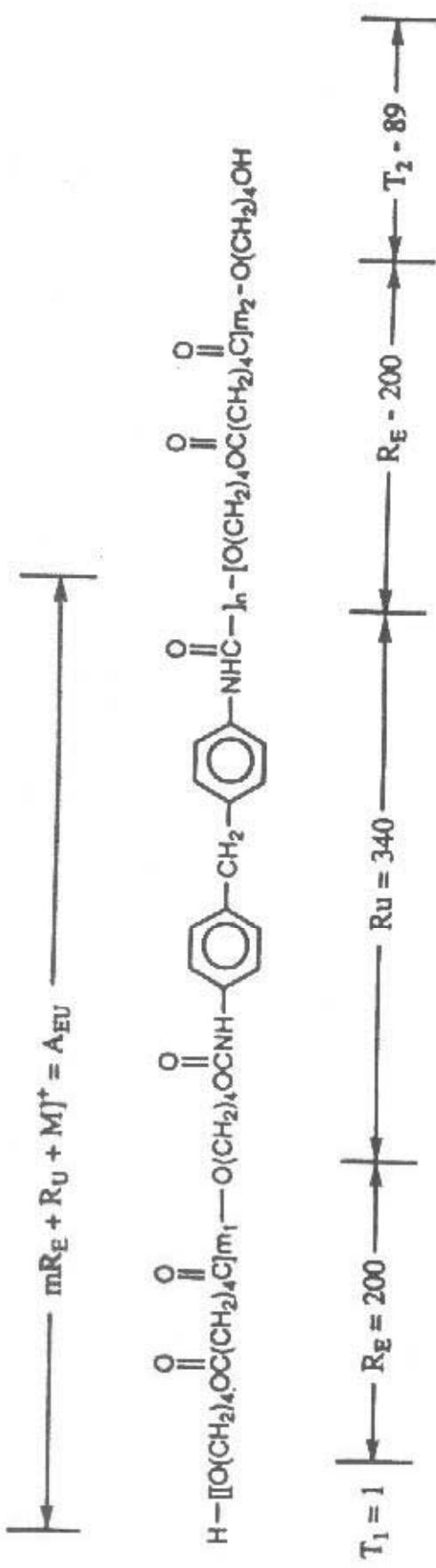




**Relative intensities of the R_n and $R_n - \Delta$ clusters
vs.
PI chain length**



POLYURETHANE STRUCTURE



**Polybutylene Adipate
4',4' -Diphenylmethane diisocyanate**

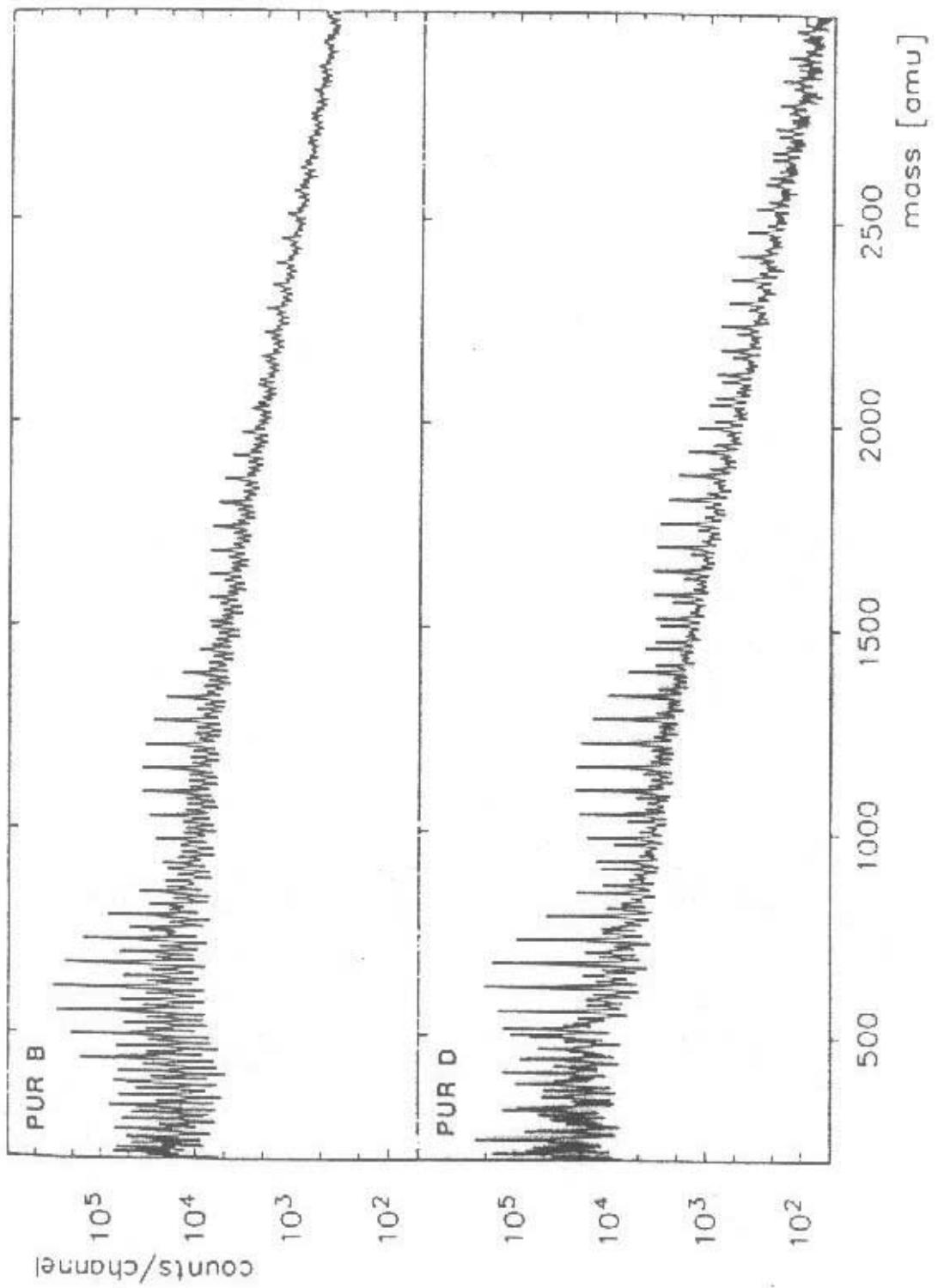
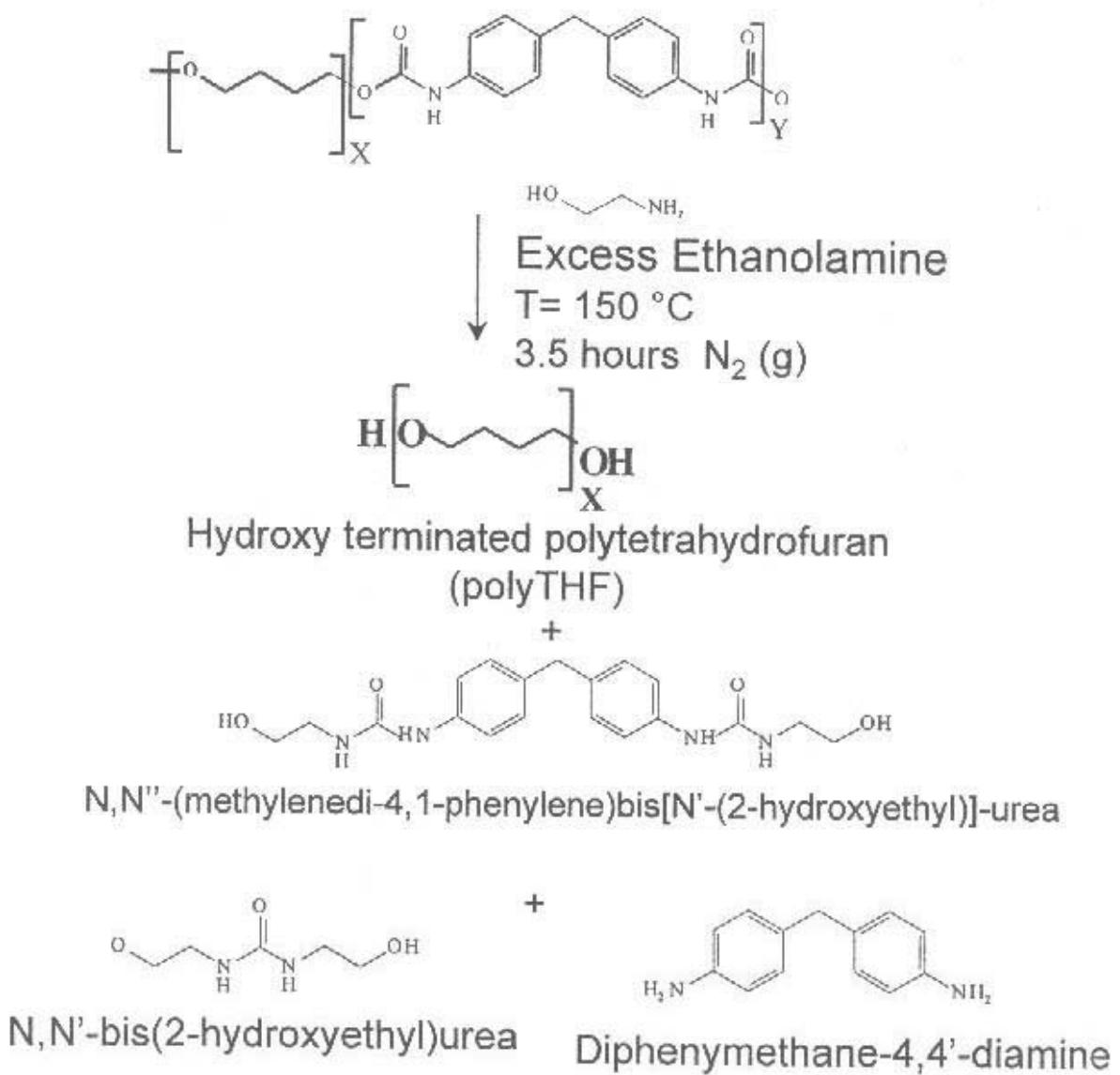
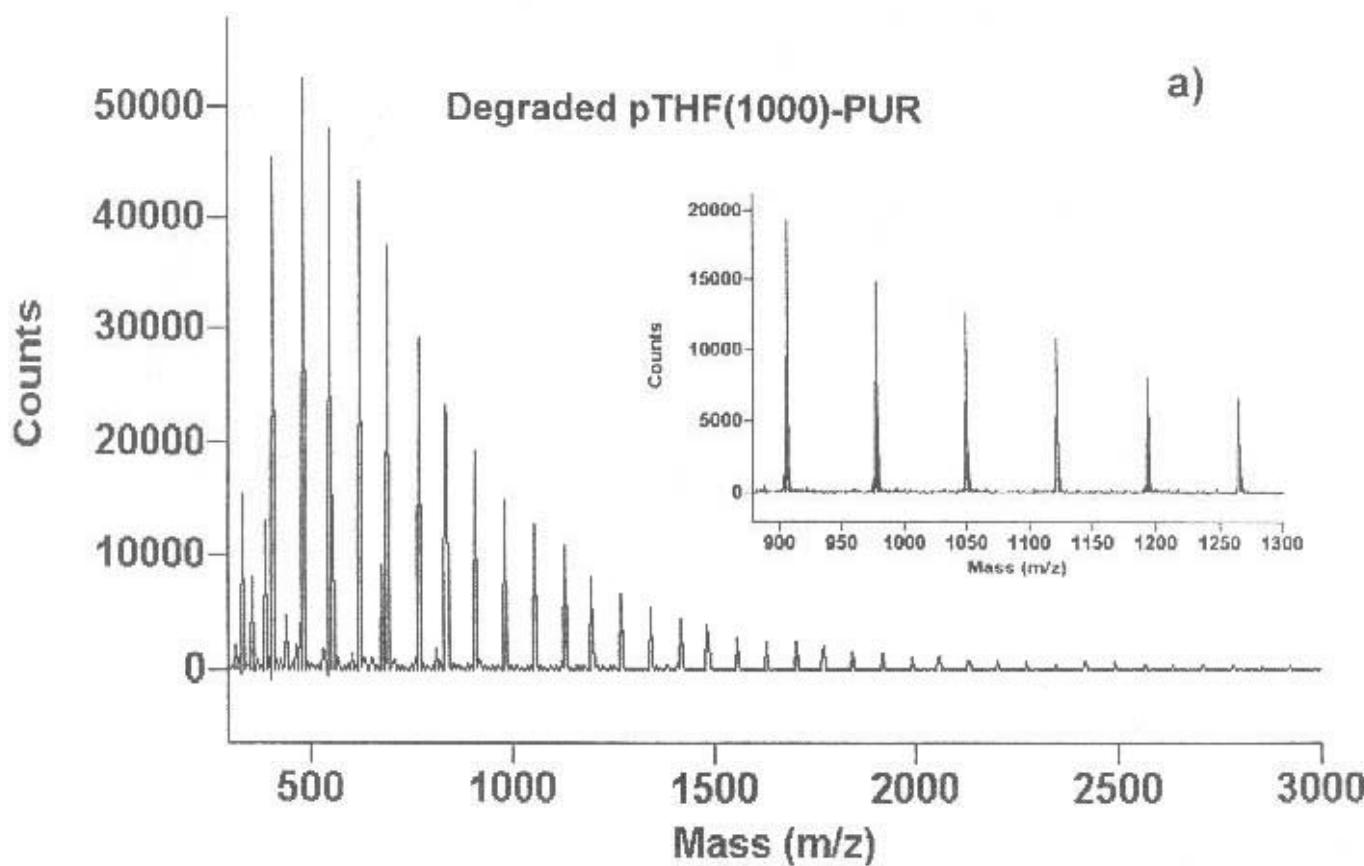
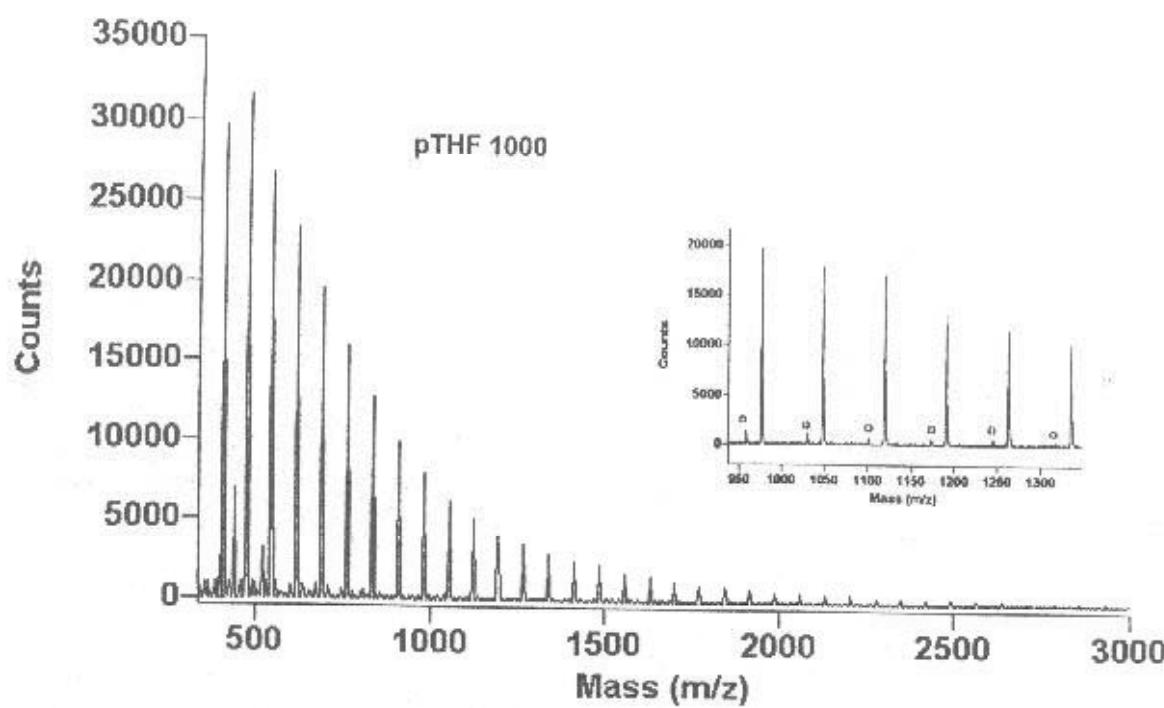


Figure 43

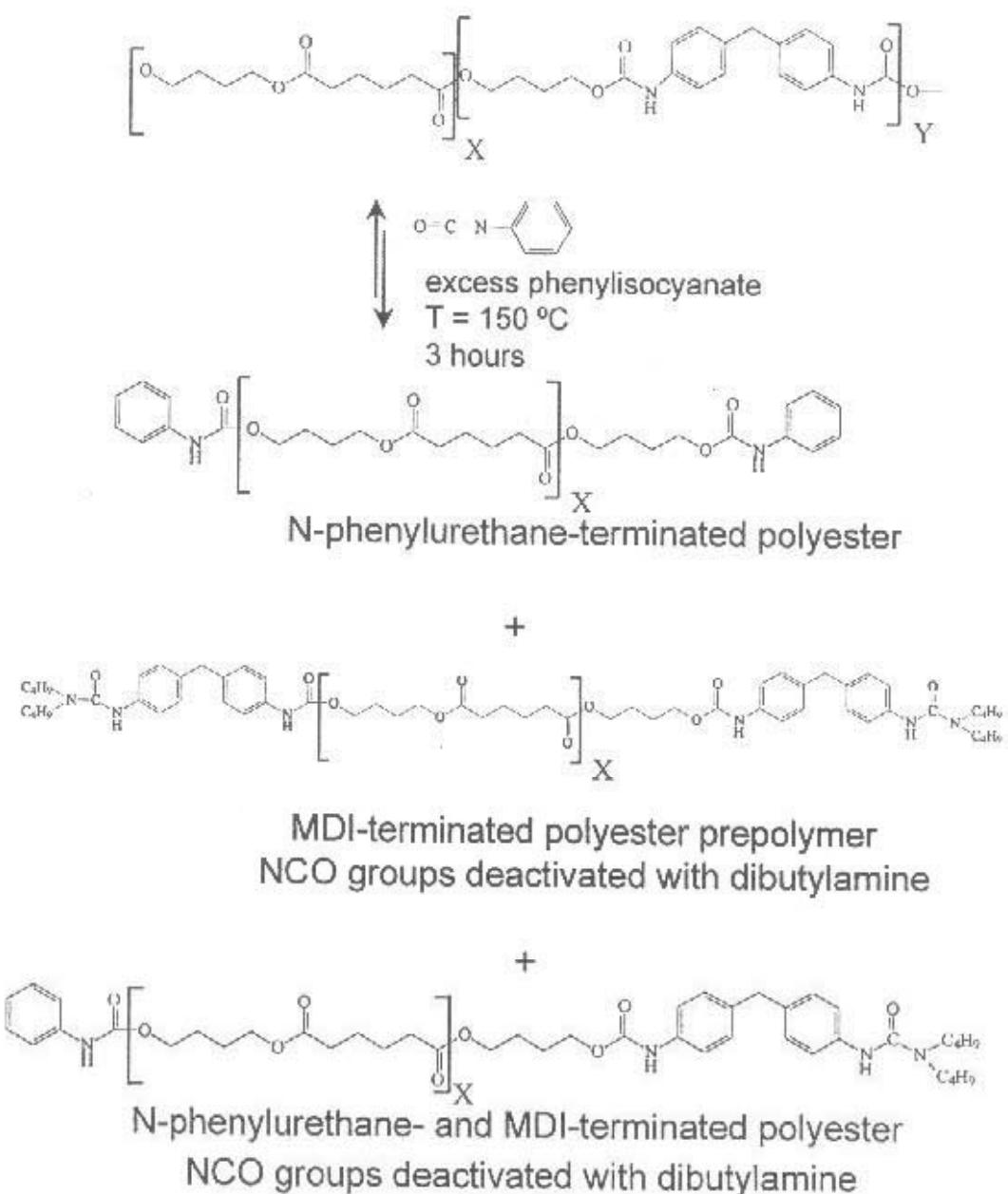
Ethanolamine degradation reaction of pTHF-PUR



Scheme 1.



Phenylisocyanate degradation reaction of pBA-PUR



Scheme 2.

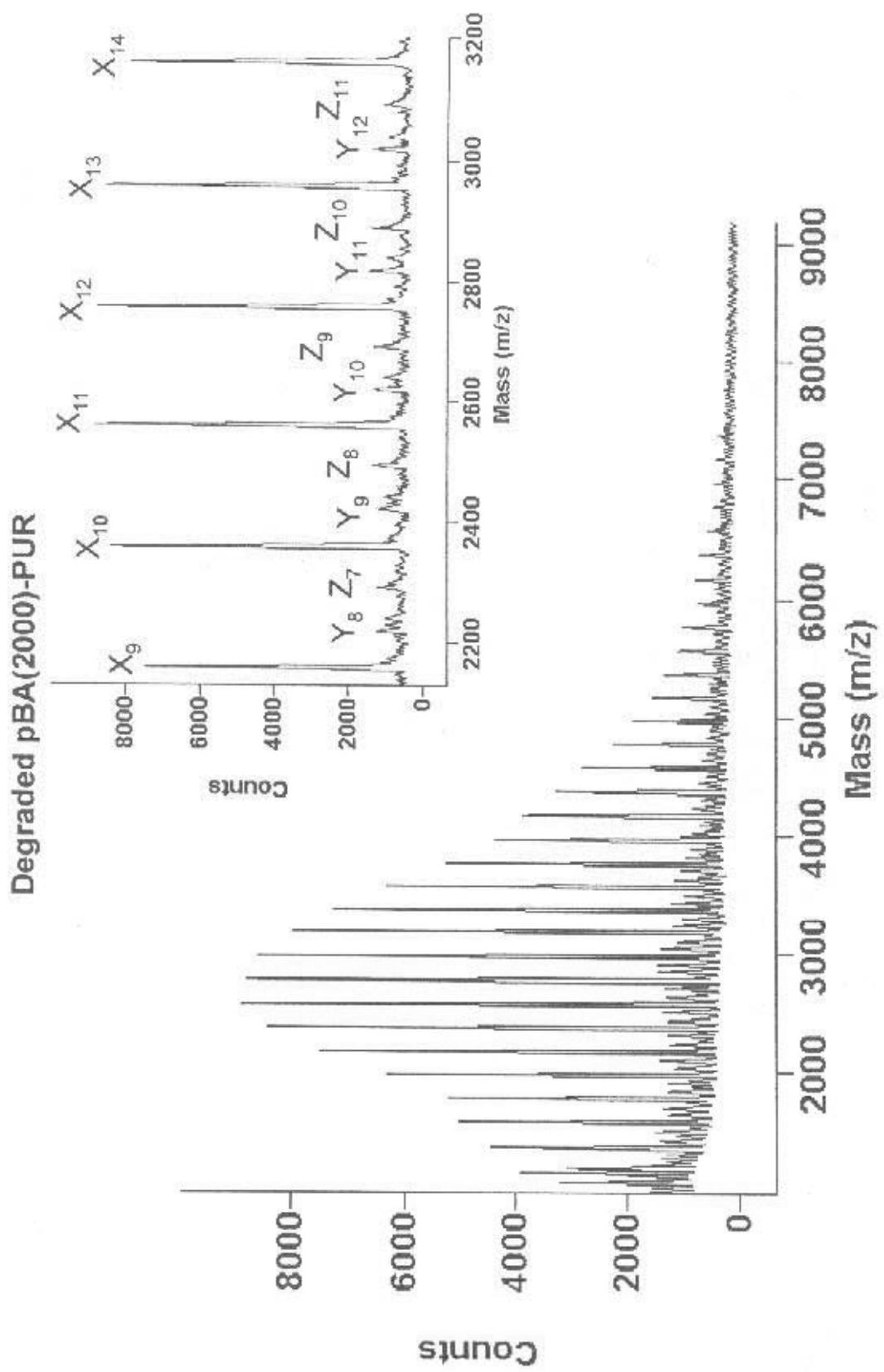


Figure 4.

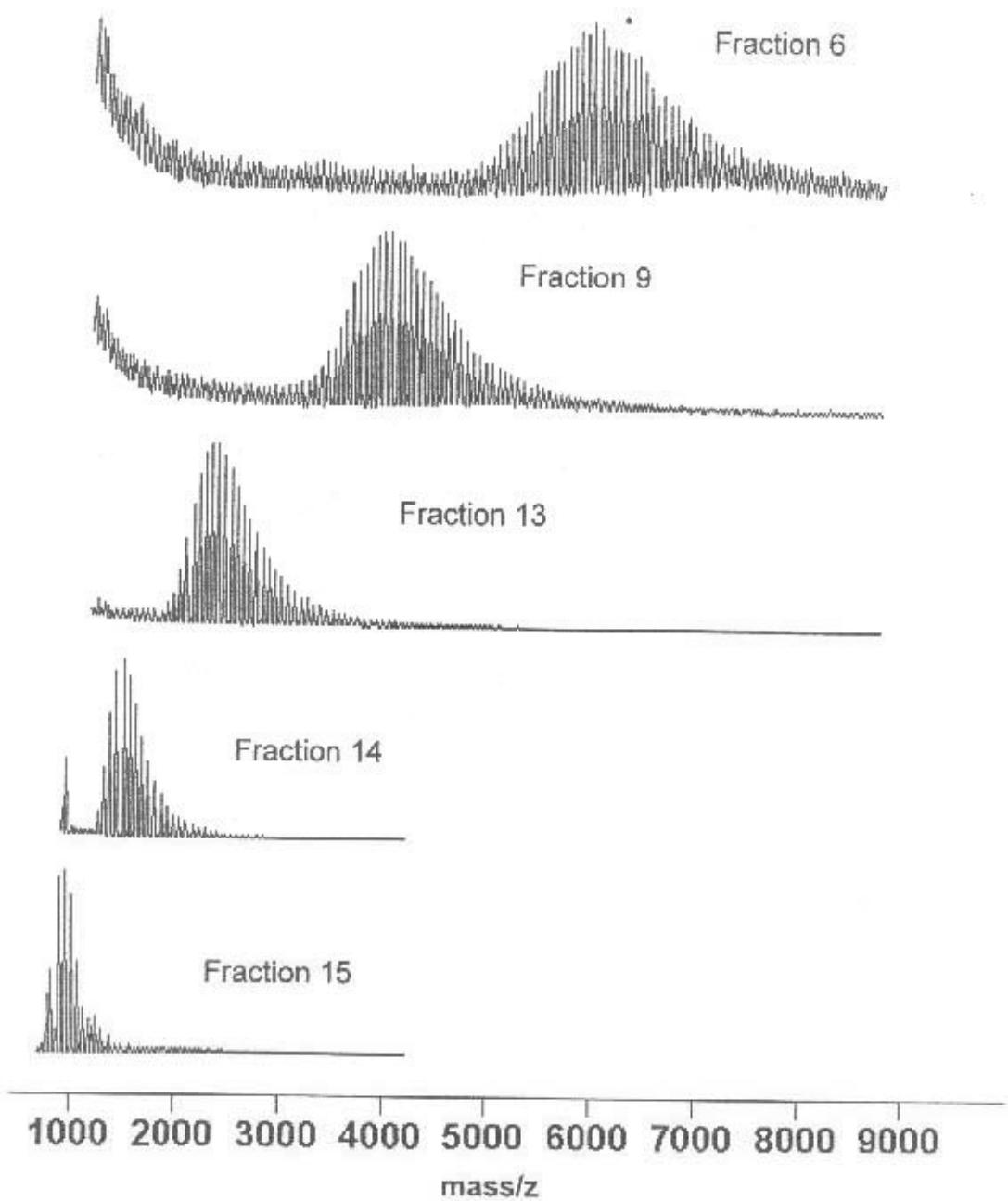
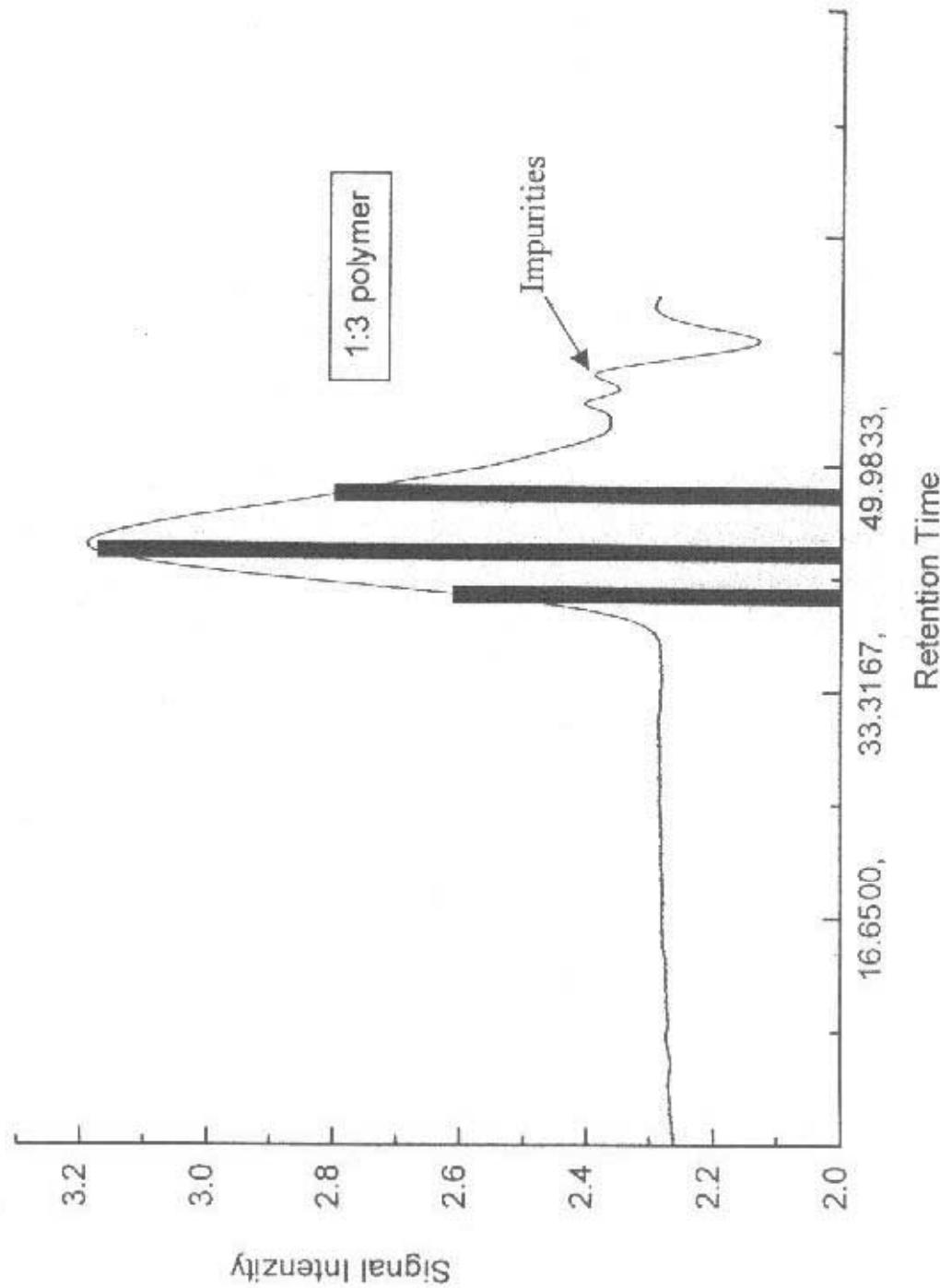


Figure 6.

GPC of pTHF PUR Soft Block



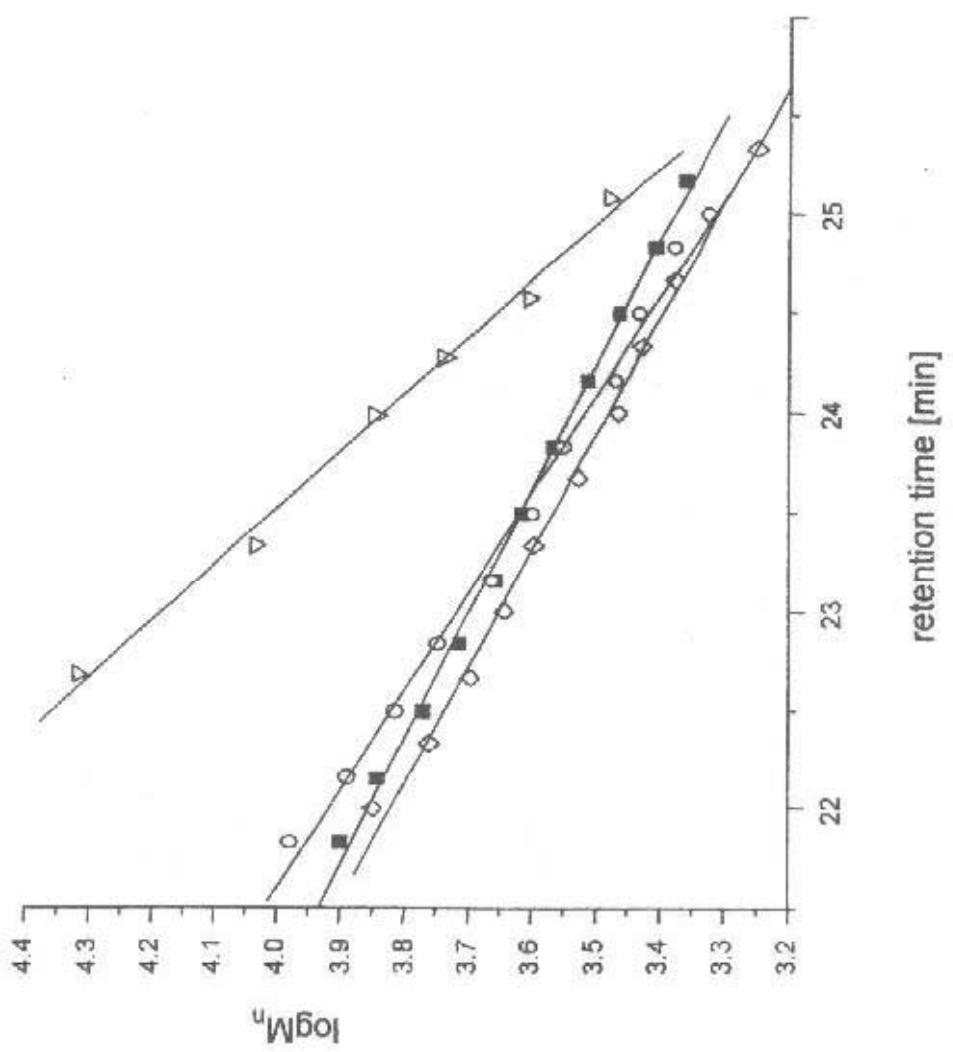
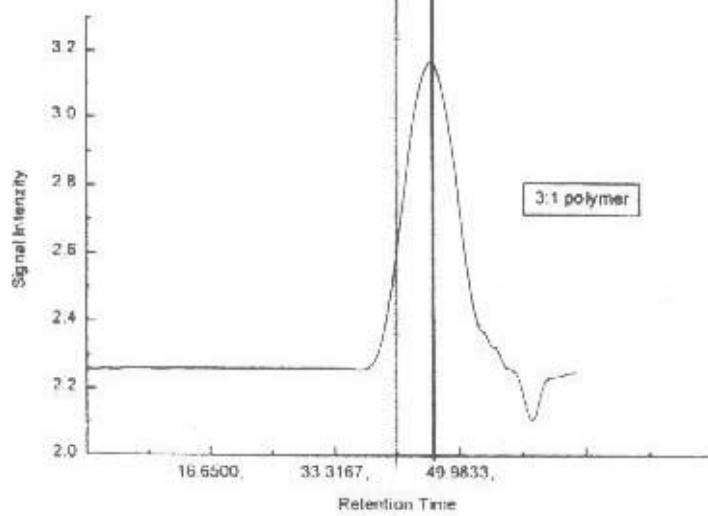
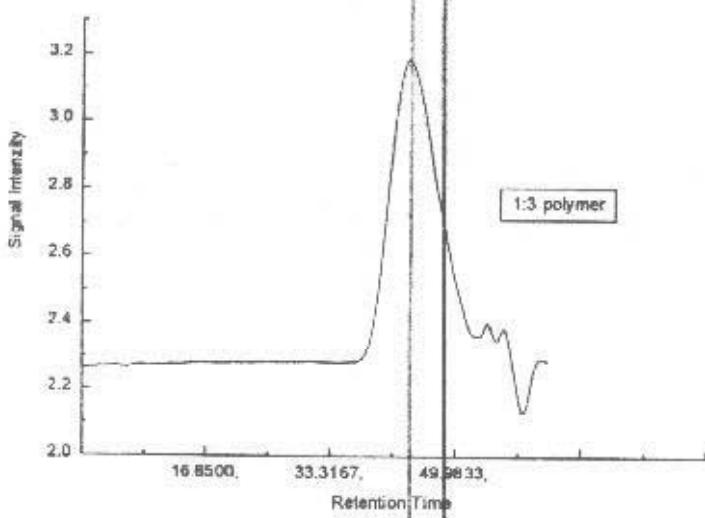
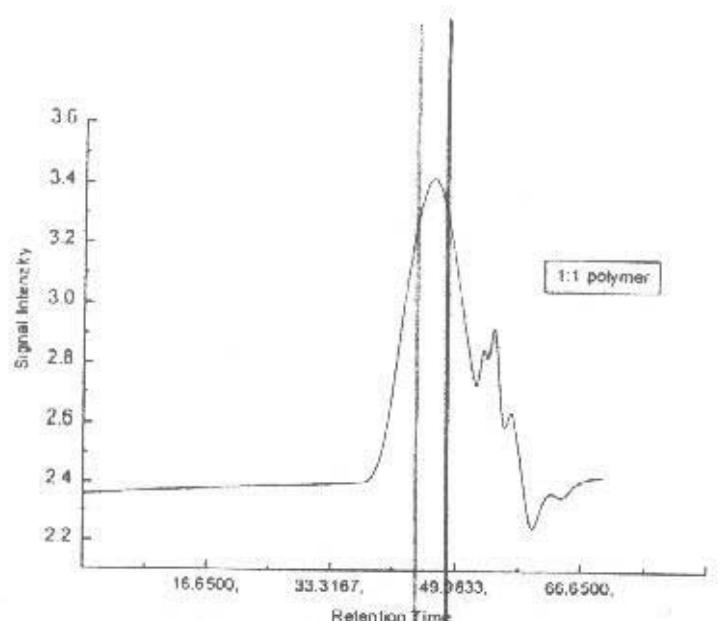


Figure 5.

Polymer	Nominal M_n	SEC-MALDI		Other Method	
		M_n	M_w	M_n	M_w
THF	2051	1873	4765	1914	2739-M
THF-PUR	2051	1779	4082	1981	2786-M
PBA	1022	1295	3303	1757	2713-M
PBA-PUR	1022	1943	3069	1817	2381-M
PBA-PUR	1000	2273	3180	2343	3187-L
PBA-PUR	4000	4349	6943	5038	7557-L
PBA-PUR	4000	2890	7322	4658	6662-L

M = MALDI

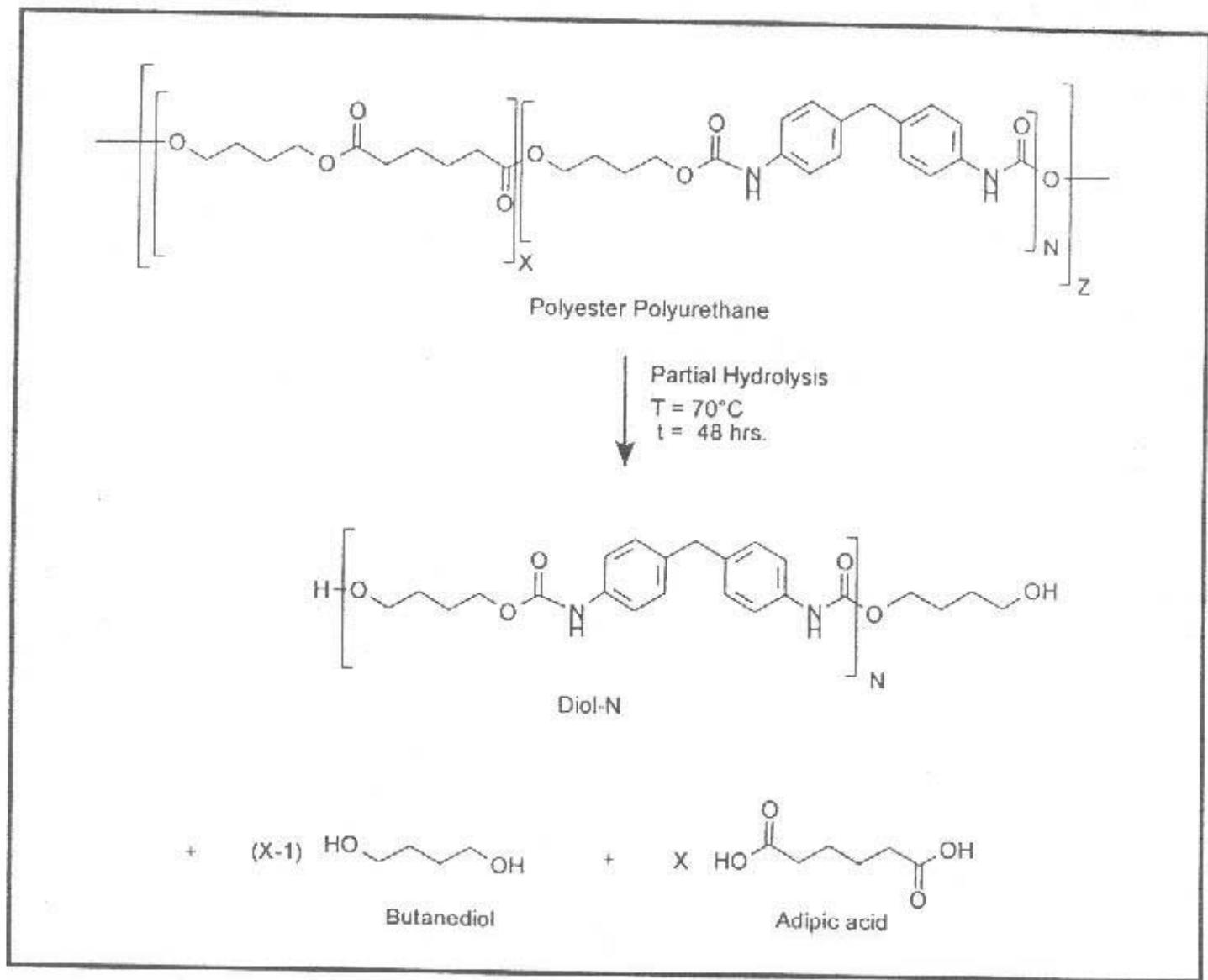
L = MALS-SEC



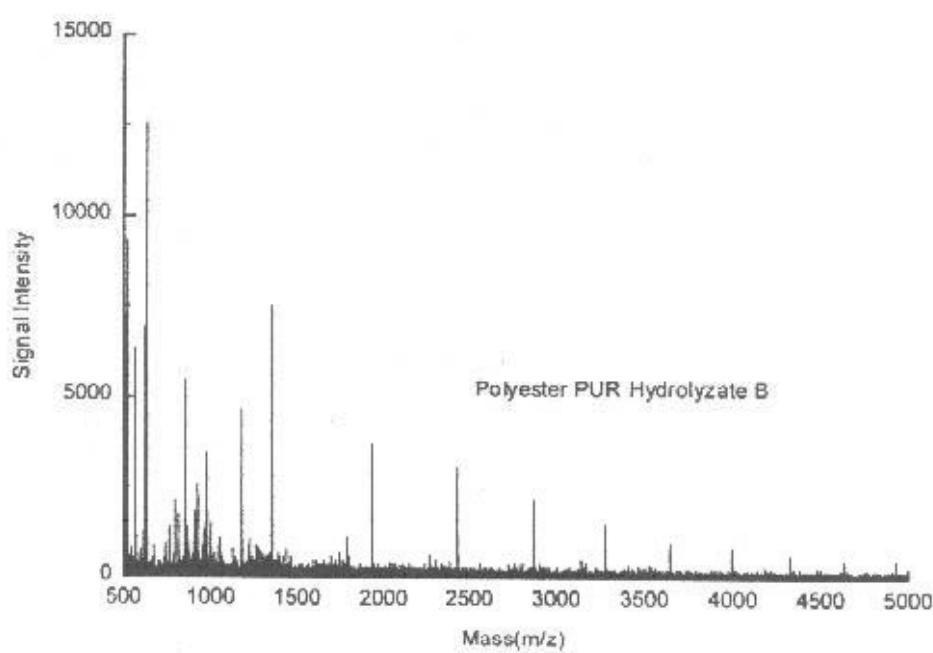
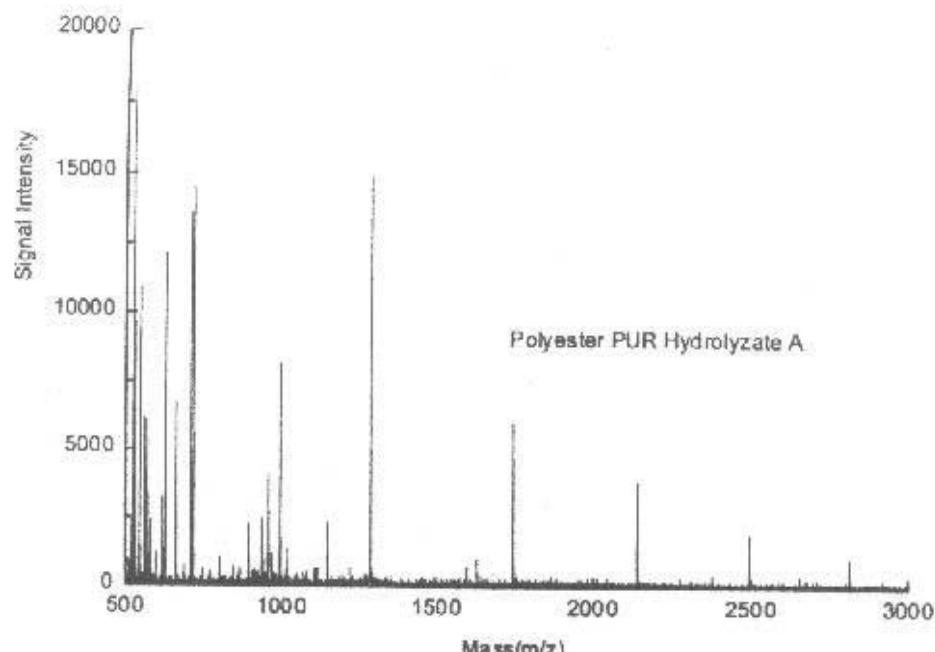
GPC traces for polyTHF based PUR degradation products

Polymer	M _n By Titration(t)	SEC-MALDI			MALDI Alone		
	Calculated M _n (#)	M _n	M _w	PD	M _n	M _w	PD
PBA 4000	3650 (t)	3456 (5.3)	5253	1.5	2815 (22.9)	3877	1.4
PBA 1000	2011 (t)	1910 (5.0)	3069	1.6	1872 (6.9)	2897	1.6
PUR 4000	-----	3515 (3.7)	6200	1.8	2956 (19.0)	4055	1.4
PUR 1000	-----	1943 (3.3)	3180	1.6	1952 (2.9)	2604	1.3
PUR 3:1*	2501 (#)	2538 (1.5)	4125	1.6	2435 (2.6)	3174	1.3
PUR 1:1*	3050 (#)	3192 (4.6)	5324	1.6	2583 (15.3)	3429	1.3
PUR 1:3*	3600 (#)	3528 (2.0)	6065	1.7	2681 (25.5)	3575	1.3

* - Ratios given are PUR 1000-to-PUR 4000

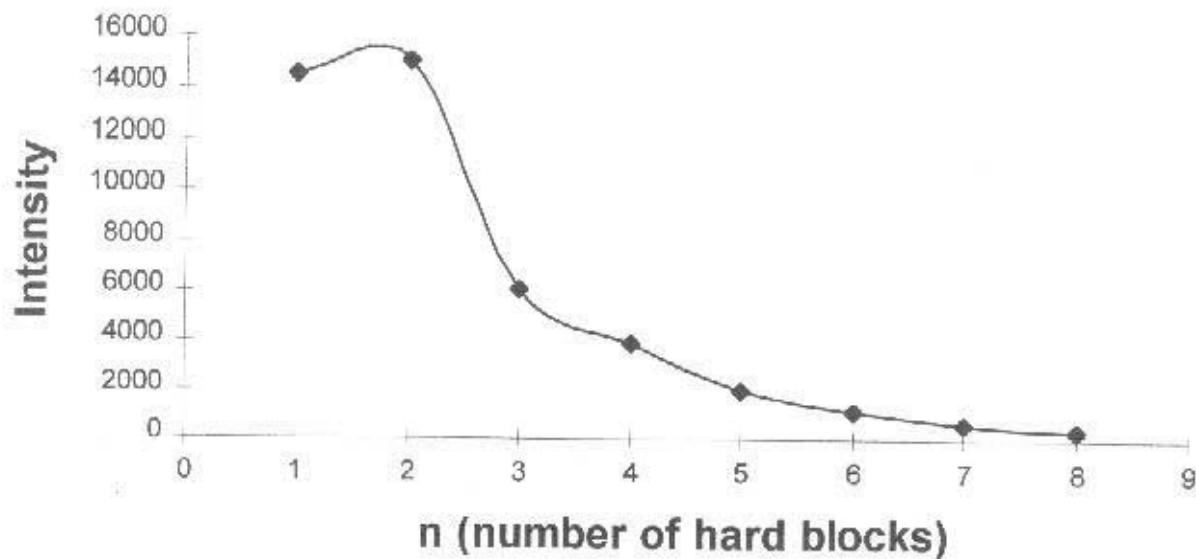


Scheme 1: Partial hydrolysis of a polyester based polyurethane (previously published in BIR 3646).

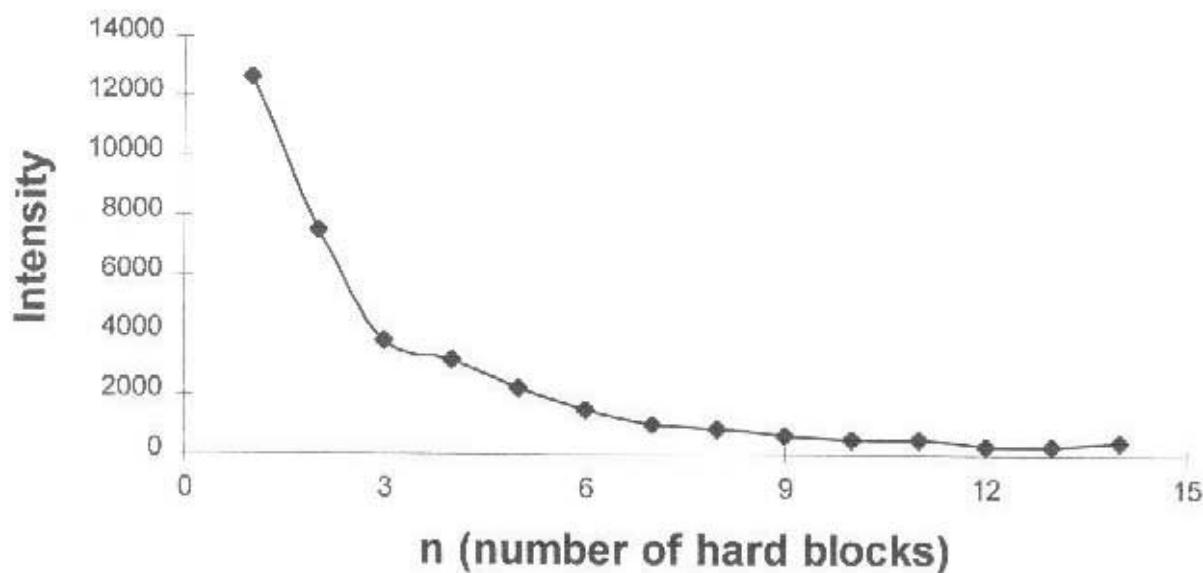


MALDI spectra of polyester PUR hydrolyzates,
showing series of hard block (MDI) peaks separated
by 340Da up to m/z of 5000.

Hydrolyzate A



Hydrolyzate B



MALDI intensity vs. number of hard blocks in polybutylene adipate PUR samples.

QUANTITATIVE ANALYSIS BY SIMS AND/OR MALDI

DIRECT – FORGET IT!

REPRODUCIBILITY IS THE PROBLEM

MATRIX

SOURCE

SO WHY BOTHER?

1. Sensitivity
2. High Mass
3. Small Samples
4. Speed
5. Macromolecules

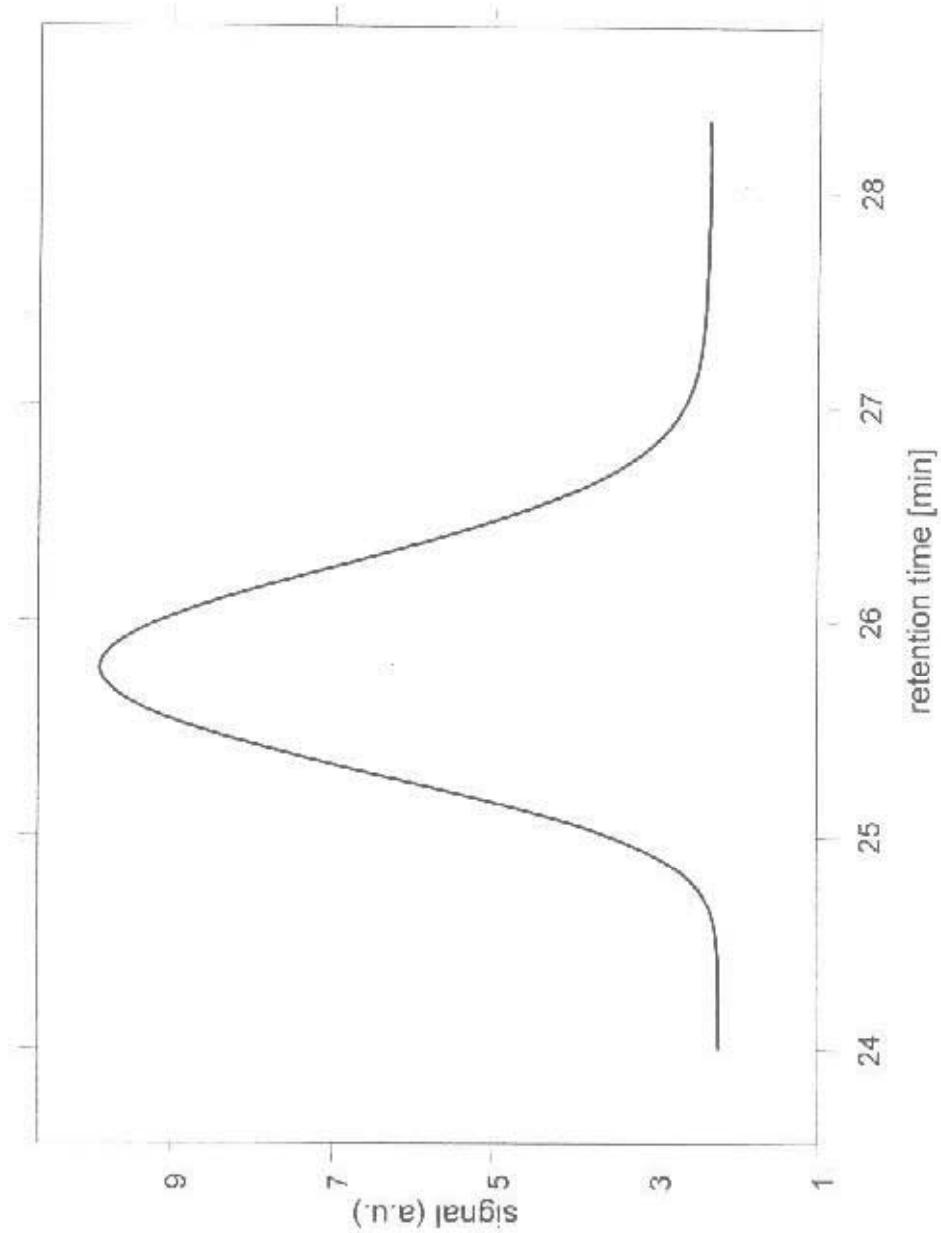


Figure 1.

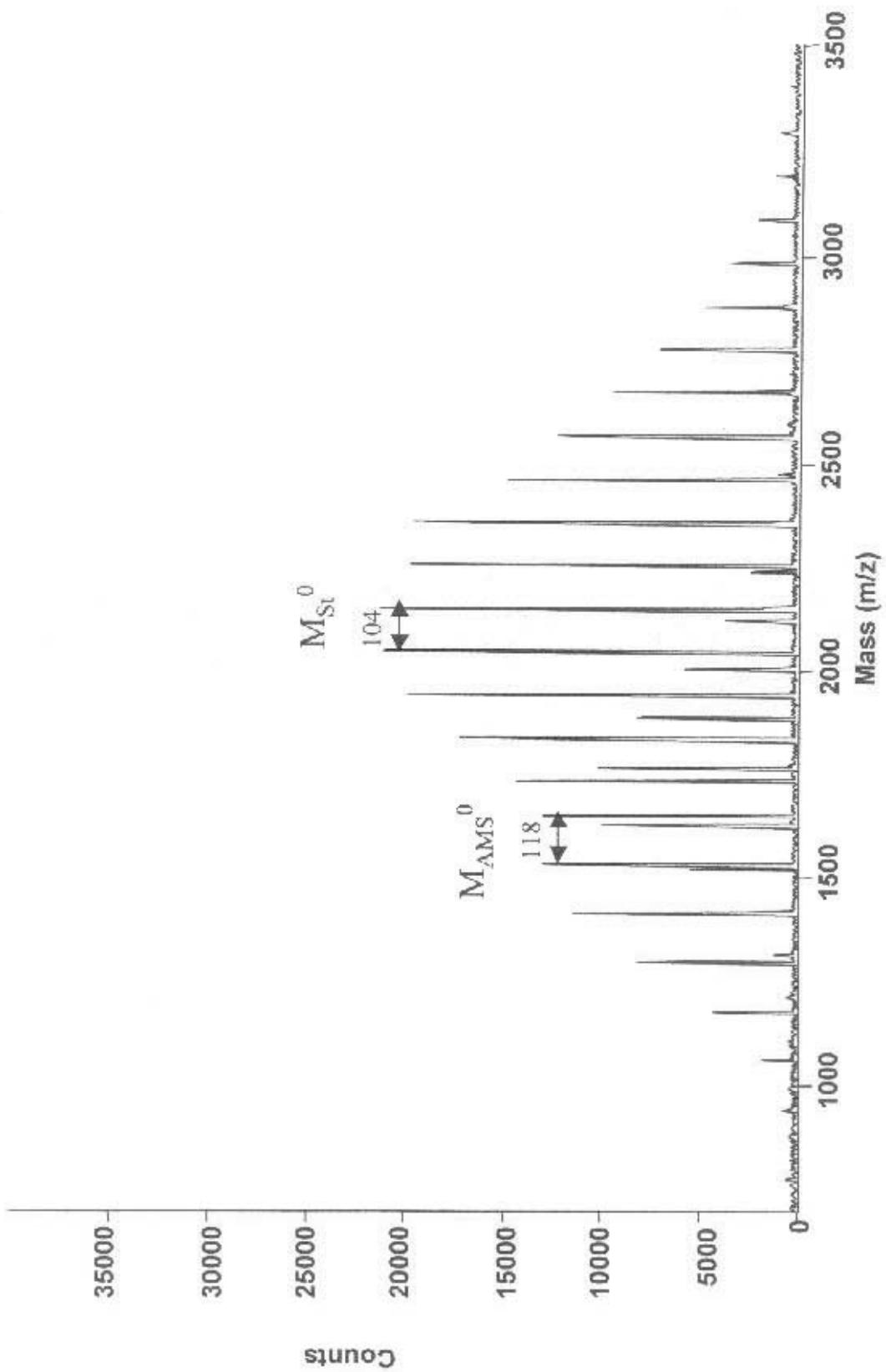


Figure 2.

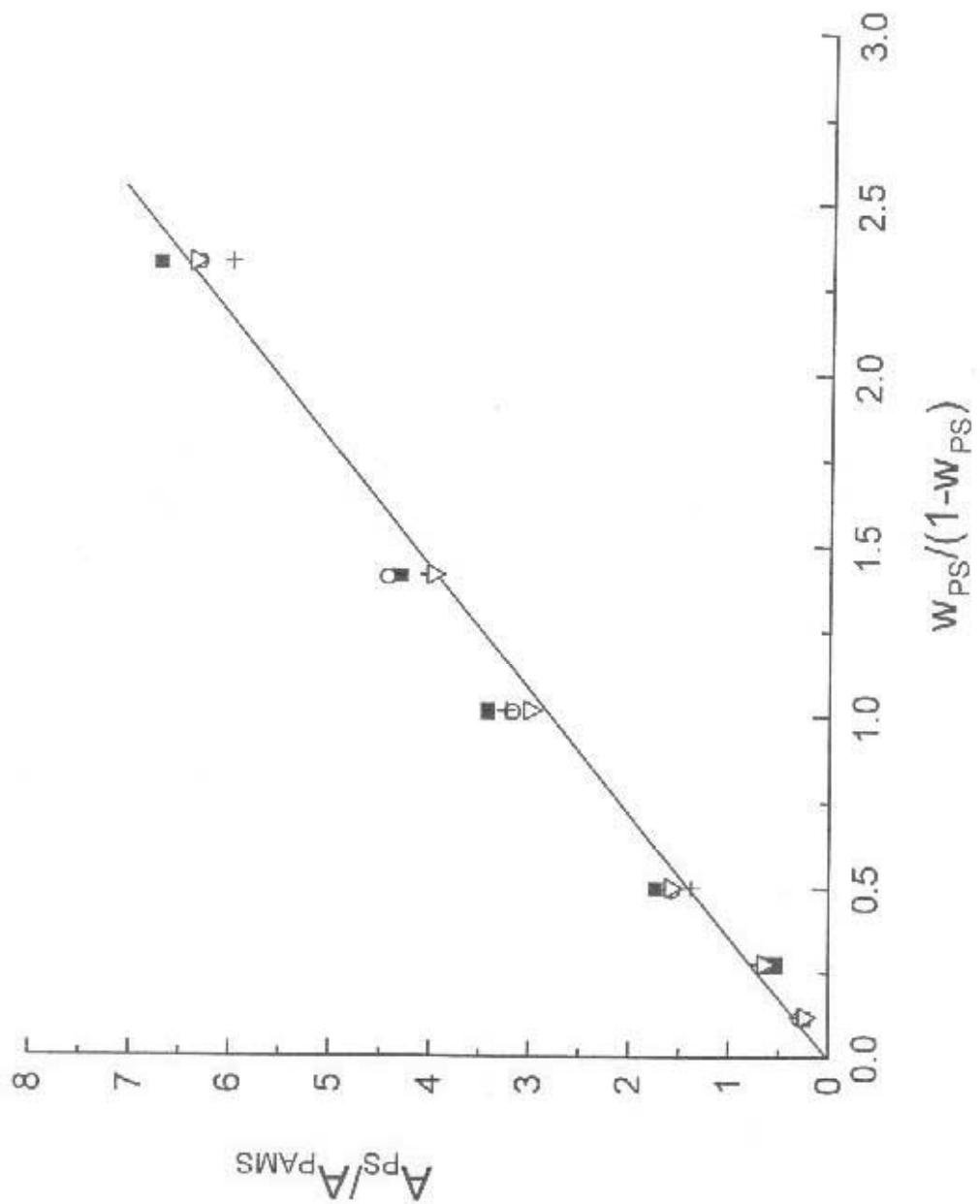


Figure 6.

